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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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TECHNICAL PROGRESS REVIEWS

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

FALL 1964

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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

New Contractor for Hanford Laboratories

The Atomic Energy Commission (AEC) has selected as a basis for negotiations a proposal from Battelle Memorial Institute to operate the Hanford laboratory facilities at Richland, Wash. The transfer of laboratory operations from General Electric Company to the new contractor will begin as soon as practicable and is expected to be complete this year. The laboratory now employs 1800 persons or about 22% of the total plant employment at the Hanford site.[1] Battelle plans to build a number of new facilities at Hanford to support the present laboratory complex and has set up temporary offices at Richland, Wash., and a project development office in Portland, Oreg.[2] The general plans for commercial development at the Hanford site were discussed in the previous issue of *Reactor Fuel Processing*.[3]

Further Reduction in U.S. Production of Enriched Uranium

In accordance with a decision of the President of the United States, AEC[4] will put into effect over the next four years further reductions in the rate of production of enriched uranium, beyond the 25% curtailment for fiscal year 1965 announced in the State of the Union Message on Jan. 8, 1964. This reduction for the period following fiscal year 1965 was recommended by the Commission as being indicated by further study of the projected requirements of the Department of Defense. The planned reduction would still assure adequate supplies of enriched uranium for both military and civil uses.

To accomplish the additional curtailment, AEC will reduce the electric power usage in its gaseous diffusion plants. When these reductions are made, the overall decrease in production of enriched uranium will be 40% below production at the 4850-Mw level (which was the previously planned level to be reached on July 1, 1964).

The new cutbacks will be made at the plants at Portsmouth, Ohio, and Oak Ridge, Tenn. Operations at the Paducah, Ky., diffusion plant will not be affected.

The power curtailment will not affect existing AEC commitments for the purchase of uranium concentrates, nor will it result in further cutbacks at the AEC uranium feed processing plants.[4]

Public Liability Insurance for a Private Fuel-Processing Plant

Before a license is issued for operation of a private chemical processing plant for nuclear fuel, the law requires that the licensee furnish financial protection, in an amount determined by AEC, to cover public basic liability claims. The first such plant is the one now under construction and scheduled to be operated by Nuclear Fuel Services, Inc. (NFS), in 1965.

AEC has proposed[5] to establish this amount, on an interim basis, at $20 million for operation of the plant and $5 million for the period when irradiated fuel elements are being stored on the site before operation. These sums are to be provided by NFS in the form of public liability insurance or other financial protection. Once such financial protection is provided, AEC must furnish indemnification of the licensee up to $500 million, to cover liability claims in excess of the amount of the above financial protection. The Commission would charge NFS $4000 per year for government indemnity.

Firm criteria have not yet been established for the required financial protection for fuel-

processing plants of various types, and AEC is still considering the factors involved and the public comment on this interim proposal.[5,6]

Savannah River Plant To Accept Delivery of Highly Enriched Reactor Fuel for Processing

At the present time there are no commercial chemical processing services available for irradiated nuclear fuels, and only AEC plants have been available to provide this service to operators of nuclear reactors. On this plan, highly enriched fuels could be delivered for processing only at the AEC-owned Idaho Chemical Processing Plant (ICPP) near Idaho Falls, Idaho. Now, the AEC Savannah River Plant near Aiken, S. C., has been designated as an optional delivery point for highly enriched fuel.[7] (The Savannah River Plant will continue to be the receiving site for fuels with low and intermediate enrichments of ^{235}U.) In all cases the operator is required to make financial settlement with AEC for processing services when delivery is made. AEC plans to withdraw these services as commercial services at reasonable prices become available.[7,8]

Modified Assignments for Processing of Government Nonproduction Fuels

Although the Savannah River Plant is now authorized to accept fully enriched-uranium-aluminum alloy fuels [Materials Testing Reactor (MTR) type] from licensed domestic reactors and foreign reactors, the AEC Division of Production has requested that government fuels of this type continue to be shipped to the ICPP in order to balance the processing loads at both sites. The newly modified assignments for chemical processing of government nonproduction fuels are the following:

1. Highly enriched-uranium fuel elements of aluminum alloy (MTR type) and zirconium alloy (Navy type) should be shipped to the ICPP for processing.
2. Highly enriched-uranium fuel elements and those intermediate-enrichment fuel elements of stainless-steel cermets (Army type) and Hastelloy X and Nichrome alloys should be shipped to Savannah River for processing.
3. All natural and low-enrichment and intermediate-enrichment fuel elements, including thorium fuels, should be shipped to Savannah River for processing.

However, when cost considerations appear to favor shipping government fuels of the MTR type to Savannah River rather than to Idaho, the Division of Production will consider authorization of such shipments on the basis of individual cases.[9]

Firms Offering Fuel-Cycle Services

A survey[10] of fuel-cycle services by American companies has been recently published. The service categories and the number of firms listed in each category are the following:

1. Fuel processing (of feed material into fuel-grade material): 17 firms
2. Processing of irradiated fuels: none (one plant under construction)
3. Fuel fabrication: 19 firms
4. Waste disposal: 7 firms
5. Spent-fuel transportation: 7 firms

A detailed discussion of each category is given in the original article.

Nuclear Fuel Materials Plant in Oklahoma

Kerr-McGee Oil Industries, Inc., announced that it is beginning to build a $1.5 million fuel-materials processing plant near Oklahoma City.[11] The plant will enable the company to convert bulk quantities of low-enrichment UF_6 into UO_2 and uranium metal. It will also have a uranium-scrap recovery operation. Equipment from a smaller processing plant at Cushing, Okla., which Kerr-McGee purchased two years ago, will be moved to the new site. Kerr-McGee is also a producer of U_3O_8 from ores.

Design of Fuel-Processing Plant in Japan

The Japan Atomic Fuel Corp.[12] has awarded a $225,000 contract to AMF Atomics for designing chop-and-leach head-end equipment for its proposed nuclear fuel-processing plant, which will be the first fuel-processing plant in Japan. The equipment will be similar to that which AMF is manufacturing for the NFS plant in western New York. Three other companies that have roles in designing the Japanese plant are Nuclear Chemical Plant, Ltd. (Britain), which has responsibility of overall design; St. Gobain Nucleaire (France); and Weinrich and Dart (United States).

Proposed Legislation Discussed Before the U. S. Joint Committee on Atomic Energy

Issues pertinent to proposed legislation which would implement private ownership of nuclear fuels were discussed at hearings before the U. S. Joint Committee on Atomic Energy.[13] Representatives of AEC were reported to have brought forward the following proposals for consideration.

1. Deferment of toll enrichment services until Jan. 1, 1969, in order to reduce the size of the government's uranium stockpile, which is affected by the recent 40% cutback in ^{235}U production for weapons.

2. Discontinuation of the leasing of nuclear material generally on Jan. 1, 1971, instead of June 30, 1973, with possible exception in the case of advanced reactor types.

3. Prohibition of enrichment in U. S. gaseous diffusion plants of foreign ore for use in domestic reactors until July 1, 1975.

Issues pertaining to these proposals were discussed at the hearings by congressmen and spokesmen for AEC and private firms with nuclear interests.

Economics of Nuclear Fuel Cycles

Comparison of Integrated and Centralized Fuel-Processing Plants

Alternative schemes for processing in nuclear fuel cycles are (1) integrated or "closed-cycle" operation with a combined facility which includes the nuclear reactor and the fuel-processing and fabrication plant and (2) separated reactor and processing facilities, the latter type of plant serving a number of reactors. The centralized processing plant (separate from the reactors) entails shipping of new and spent fuel to and from the reactors. Such shipping of radioactive materials presents costs that are not encountered in an integrated facility. The integrated processing approach is being developed and demonstrated for the Argonne National Laboratory (ANL) plutonium-fueled fast reactor (EBR-II) at Idaho and for the thorium-uranium fuel cycle by the PCUT program (in Italy). The PCUT (Programme Ciclo Uranio Thorio) processing facility was designed for use with the Elk River reactor and could also process the fuel elements from the SENN reactor if this reactor were converted to the thorium fuel cycle.

An economic comparison[14] of integrated and centralized processing facilities has been made by the Atomic Energy Division of the Allis-Chalmers Mfg. Co., which has technical responsibility for the PCUT program. The results of this study indicate that unit costs of processing spent fuel in an integrated processing facility for a single 1000-Mw(e) reactor are competitive with those of a central processing facility serving five such reactors. Integrated reactor-processing systems of larger size show enhanced economic advantage. A shipping cost of $15 per kilogram of irradiated fuel was used in this study.

Fabrication costs were also considered in this report. However, fabrication costs were said to show virtually no relation to plant load because of the "piecework" nature of fabrication of the oxide fuel considered in the reference process. Fabrication costs of $96 per kilogram of fuel and shipping cost of raw fuel material of $3/kg were cited in the study.

Although specific cases analyzed in this study were based on oxide-fueled thermal reactors using the uranium-thorium and uranium-plutonium fuel cycles, the report considers that the main result can be generalized to the case of fast reactors of the uranium-plutonium fuel cycle. In the fast reactor case, expected higher burnups tend to be less favorable to central (separate) processing facilities because of (1) the smaller quantities of fuel to be processed (i.e., the lower benefits of large-scale operation) and (2) the increased shipping costs due to the "hotter" spent fuel.[14]

Comparison of the Value of Plutonium and Uranium Isotopes in Fast Reactors

In the future, when fast reactor power stations may be in widespread use, plutonium will be a marketable commodity with a price determined by the laws of supply and demand. An estimate[15] has been made of the upper limit which an owner of a fast reactor could afford to pay in the particular case that the nearest competitor has a similar fast reactor that is fueled with enriched uranium instead of plutonium. In this study a value for plutonium is determined which makes the price of electricity the same

for either plutonium or enriched-uranium fuel, on the assumption that these fuels would be interchangeable in a fast reactor station without change in capital or operating costs. Plutonium values derived on the basis of this limited approach are relevant to the economics of a power-station network based on a mixture of reactor types. In particular, such values are basic to estimates of fuel depletion charges, inventory costs, and plutonium credits in fuel-cycle operations.

The analysis was performed by the Atomic Energy Establishment at Winfrith, England, for an oxide (cermet) reactor and for carbide-fueled reactors of various sizes, using available cross-section values for uranium and plutonium isotopes of interest. Worths of the various isotopes were calculated on the basis of maintaining criticality in fast reactors. Worths are different for various isotopes, but for large (2500 liters) fast reactors, there is little variation with fuel type, i.e., carbide, metal, or oxide fuel.

A generalized basis of fuel reactivity for the economic evaluation was provided by development of breeding gains and burnups with reference to "equivalent ^{239}Pu" performance for individual fuel isotopes. Equilibrium atomic compositions for recycled fuel are given in the report, and the approach to equilibrium is shown for both ^{239}Pu and ^{235}U startup procedures, using continuous feed of ^{238}U and recycled fuel to approach the same final equilibrium. Fuel-processing costs were assumed to be the same for all cases and were not involved in this analysis.

CASE 1

In this case the relative values of ^{235}U and ^{239}Pu (on an equivalent reactor basis) are considered on the basis of the capital costs only of the original fueling of the reactor and neglect any possible value of the bred plutonium. From the reactivity worth equivalents developed in this report, the value of ^{239}Pu is 1.4 times the value of ^{235}U, on a weight basis. The fuel cost as a function of reactor power density and plutonium value is shown in Fig. I-1. For example, if the power density is 0.5 Mw/kg, the fuel cost for a plutonium value of \$16.8/g (^{235}U value, \$12/g) is 0.8 mill/kw-hr. The 5.5%/year interest rate and the 20-year amortization period used in this calculation are the equivalent

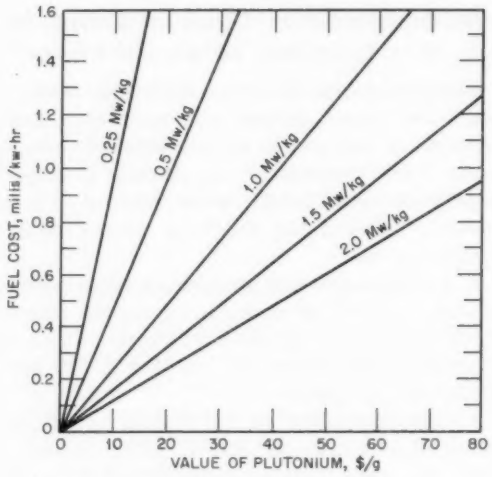

Fig. I-1 Value of plutonium to a power-producing fast reactor considering only fuel investment charges.[15]

of an annual capital-recovery factor of 0.0837 for each year of the 20-year operation. It is assumed that the reactor is self-sustaining, but no credit is taken for surplus plutonium produced. The overall rating includes load factor and out-of-reactor inventory. Thermal efficiency is assumed to be 40%.

CASE 2

In this case, credit for the excess plutonium bred is taken into account. The breeding gain G is determined on a ^{239}Pu equivalent basis for different fuel compositions and is defined as the excess ^{239}Pu produced per fission above that required to maintain reactivity. Resulting contributions of fissile-material costs as a function of breeding gain G and power density are shown in Fig. I-2. For a typical large carbide-fueled breeder, G is about 0.6 on the assumption of ideal blanket and processing behavior (no losses); for a more realistic case, including 1% processing losses and 20% losses in potential blanket breeding, G is estimated to be 0.4.

CASE 3

In this case a reference reactor was operated as a generalized converter and was fueled with either plutonium or enriched uranium in order to obtain an upper limit for the ratio of the values of ^{239}Pu to ^{235}U. When the superior breeding of ^{239}Pu is taken into account, ^{239}Pu has a

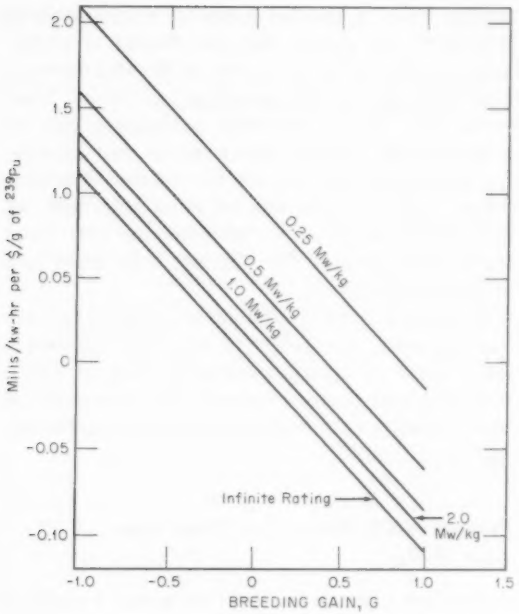

Fig. I-2 Contribution of fissile-material costs[15] in mills per kilowatt-hour per dollar per gram cost of ^{239}Pu.

value approximately 2.0 times that of ^{235}U for estimates of achievable overall rating. Since this case applies to a system containing a large number of reactors, most of which have reached equilibrium, it is not considered a realistic case for the early stages of a fast reactor program.

CASE 1

In this case, plutonium fuel values are determined for breeder reactors started up with ^{239}Pu or with highly enriched uranium, with subsequent replenishment of fuel with ^{239}Pu from the blanket. When this system is evaluated, account must be taken of the different points in time of the various charges and credits, i.e., a "present worth" calculation is made at an annual interest rate (not including amortization). Thus, if M grams of ^{239}Pu is valued at V_0 (dollars per gram) at t years after startup, the credit at startup (present worth) is $MV_0 \exp(-It)$, where I is the annual interest rate. For achievable overall ratings, ^{239}Pu has a value about 1.6 times that of ^{235}U on this basis. A summary of equivalent dollar values is given in Table I-1, on the assumption of $12 per gram of ^{235}U.

Table I-1 MONETARY VALUES FOR PLUTONIUM AND URANIUM ISOTOPES[15] RELATIVE TO A VALUE OF $12/g FOR ^{235}U

	Based on capital charges only, $/g	Breeding gains also considered, $/g
^{233}U	20	
^{234}U	1.2	1.2
^{235}U	12	12
^{239}Pu	17	19
^{240}Pu	2.5	2.9
^{241}Pu	25	29
^{242}Pu	2.5	2.5

In general, if the price of fuel is not determined by studying the economics of the nearest competitor, a price of plutonium may be obtained by comparison with the price of enriched uranium from diffusion plants. If the price of plutonium is set above a certain maximum, it becomes cheaper to start up fast reactors with ^{235}U. Pertinent relative prices are those estimated above. On the basis of overall economy, the author considers that designers should favor the lowest price of plutonium which will ensure adequate plutonium production.

Plutonium Value in Thermal Reactors

An extensive study of plutonium values in thermal reactors has been made by Hanford Laboratories.[16] Five generalized reactor types, a variety of optimized recycle fueling strategies, and several economic parameters were considered in order to make a meaningful evaluation.[17] Plutonium value in this study is defined as the price of plutonium that yields the same fuel cost for a given power-producing reactor whether the reactor is fueled with uranium or plutonium. Details of the methods and the computer codes used are given in the reports.

In $^{235}U/^{238}U$ fueled power reactors, plutonium is a by-product that can be sold, thereby lowering the (net) fuel cost of this uranium-enriched fuel cycle. In this case the higher the plutonium price, the lower will be the fuel cost. On the other hand, for the case of a plutonium-enriched fuel cycle (of the nonbreeding type considered here), the higher the plutonium price, the higher

will be the fuel cost. The common plutonium value is in effect the intersection of these two lines of price relation. The plutonium value at the intersection is sometimes called the "indifference" value to emphasize the point that fuel costs are the same whether the reactor is fueled with uranium or plutonium. The appropriate physics considerations, such as reactivities, are taken into account in the comparison of reference cases.

In this method of valuation, plutonium value is a function of uranium costs and hence of the price schedules of enriched uranium. For continued recycle of fissionable values as enrichment of depleted uranium for reactor feed, the value of plutonium chemically separated from ^{238}U must be compared with ^{235}U separated in the isotope diffusion cascade. Assuming that the plutonium recycle process includes chemical separation of the plutonium, the author asserts that economic studies based on the present schedule of prices of uranium enriched in the cascade show that the long-run value of plutonium is equivalent to the price of fully enriched uranium. The present schedule for enriched uranium is based on $30/kg as the cost of separative duty and $23.50/kg as the cost of natural-uranium feed, or $12.01 per gram of ^{235}U (in 90% enriched uranium).

Since ^{233}U is chemically separable from fertile ^{232}Th, similar calculations show that the value of ^{233}U is also proportional to the cost of fully enriched ^{235}U as an alternative. Because of more favorable nuclear properties in thermal reactors, ^{233}U has a higher value[16] than that of fissile plutonium (^{239}Pu and ^{241}Pu).

The effect of higher use charges (i.e., interest rates on plutonium inventory) is to decrease the value of plutonium. In representative cases cited, increase of the interest rate from 4.75 to 12.5% lowered plutonium values by about 15%. This reduction in plutonium value (compared to an equivalent enriched-uranium fuel) reflects the relatively high level of plutonium enrichment required to supply the neutron absorption by the fertile isotope ^{240}Pu. The capitalization structure of the economic model is also a factor.

Higher costs of handling and processing, as a result of the higher toxicity of plutonium as compared with uranium, would also tend to lower the plutonium fuel value. An estimate of $5 to $10 per pound of ^{238}U contained in the fuel was cited for the magnitude of the incremental cost of special handling for plutonium. However, the higher the enrichment of plutonium in the fuel, the lower is the incremental cost per gram of plutonium involved. Thus relatively more favorable situations can be achieved by zoning the reactor and confining plutonium enrichment to depleted uranium, where enrichments can be relatively high (of the order of 3%). In this case the estimated fabrication penalty for plutonium is about 10% relative to uranium.[17]

In general, these studies are considered under present conditions to have established a floor value of fissile plutonium of about $10/g to $12/g with an associated fuel saving of 0.3 to 0.5 mill/kw-hr over fuel costs if plutonium had no utility.[18]

Present AEC Prices for Plutonium and ^{233}U

Present base charges set by AEC[19] for plutonium and ^{233}U fuel materials of standard isotopic assays available for distribution are the following: $43 per gram of ^{239}Pu and ^{241}Pu as nitrate and $82 per gram of ^{233}U in aqueous nitrate solution. A schedule of minor reductions (less than $3/g) is also given to take care of certain variations in isotopic compositions.

The following reduced base charges are stated to apply to dollar amounts due AEC for loss or consumption of plutonium and ^{233}U under domestic lease arrangements: $10 per gram of ^{239}Pu and ^{241}Pu as nitrate, oxide, or metal; and $14 per gram of ^{233}U in aqueous nitrate solution, oxide, or metal. These reduced charges are to apply only to those cases for which AEC has determined that "the use of such material will produce technical and economic data of sufficient interest in the AEC program and the lessee has agreed to extend the AEC access to such data and appropriate patent rights." It is further stated that these reduced charges represent the estimated values of plutonium and ^{233}U as fuel in thermal nuclear reactors relative to the present schedule of base charges for uranium enriched in ^{235}U. [The ^{235}U schedule was reported in *Reactor Fuel Processing*, 5(4): 4 (October 1962).] If the ^{235}U schedule is revised by AEC, the above figures of $10 and $14 are to be adjusted proportionately. Details of specifications for chemical forms, impurities, and shipping are also given. (W. J. Mecham and A. A. Jonke)

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Since a commercial fuel processor is now expected to handle the majority of U. S. power-reactor fuels, government-sponsored process development work in the area of aqueous processing has diminished markedly. Treatment of plutonium fuels and highly refractory fuels, and processing of heavy elements other than plutonium and uranium, remain of interest. New and improved plant equipment continues to be developed.

Preparation of Fuels for Recovery

Slow dissolution of highly irradiated alloy fuels, complications accompanying dissolution of plutonium dioxide, and a modified process method for graphite and carbide fuels are discussed.

Dissolution of Highly Irradiated Aluminum Alloy Fuels

In two recent reports[1,2] it is noted that, when binary alloys of aluminum with uranium and plutonium are highly irradiated, they become very difficult to dissolve in mercury-catalyzed nitric acid. This reagent rapidly dissolves unirradiated alloys (containing about 7% uranium or plutonium) and those moderately irradiated (to burnups of 20 or 30% of the uranium or 60% of the plutonium). In both instances it was recommended that the aluminum phase be dissolved in caustic followed by dissolution of the residue in nitric acid in order to obtain overall dissolution rates suitable for plant application.

Rohde[1] notes that complete solution of wafers of Chalk River-irradiated (45% burnup) highly enriched uranium-aluminum alloy in boiling 4*M* to 6*M* nitric acid containing 0.005*M* to 0.05*M* mercuric nitrate required 40 to 50 hr in laboratory studies. This corroborated plant experience with similar materials which required much-prolonged batch dissolution times and repeated contacts with acid. With boiling 5*M* sodium hydroxide, the aluminum matrix was dissolved in 1 to 4 hr, and the residue could then be readily dissolved in nitric acid.

A report by Perkins of work at Savannah River[2] is concerned with dissolving aluminum-clad plutonium-aluminum alloy (7% plutonium before irradiation) in preparation for plant processing. It was earlier reported[3] that, with burnup of 60% of the initial ^{239}Pu content, this alloy dissolved at rates of 10 to 20 mg/(min)(cm^2). When an aluminum-clad plutonium-aluminum alloy was irradiated to a burnup of greater than 99% of the ^{239}Pu, the cladding dissolved at a normal rate, but the average dissolving rate of the core in 7*M* nitric acid with 0.005*M* mercuric nitrate was only 0.5 mg/(min)(cm^2). This rate was not increased by increased catalyst concentration, by dipping the alloy in concentrated mercuric nitrate, by scratching the alloy surface, or by adding up to 0.06*M* hydrofluoric acid. Annealing the alloy at 500°C increased the dissolution rate somewhat but was considered to be impractical. It was possible, however, to dissolve the aluminum in the alloy in 1.8*M* to 2.6*M* sodium hydroxide, containing 2.5*M* to 3.1*M* sodium nitrate to minimize hydrogen generation, at rates of 12 to 16 mg/(min)(cm^2). The residue was then dissolved in about 2 hr by neutralizing the solution with concentrated nitric acid and boiling with a slight excess of acid to yield a final solution acidity of 0.9*M* to 1.9*M*. Very little plutonium or other alpha activity dissolved during the caustic treatment. It was thought possible, therefore, that the residue could have been

filtered off and dissolved separately without significant loss.

The pilot-plant dissolution of about 42 kg of similar plutonium-aluminum alloy, with plutonium burnup of 87 to 99%, in 6*M* nitric acid containing 0.05*M* mercuric nitrate and 0.03*M* fluoride is reported by Brooksbank and McDuffee.[4] This operation was part of the transuranic-element recovery program and provided feed solutions for ion-exchange processing. A multiple batch heel type procedure was followed in which several rods of a total of 32 were charged and digested initially with a batch of acid, followed by charging additional fuel rods and acid until the supply of rods was exhausted, and then digesting the heels with additional batches of acid as required until dissolution was complete. Confirming the Du Pont data, the average dissolution rate was indeed very slow [typically 0.7 to 0.8 mg/(min)(cm^2)], and the entire quantity required a dissolution time of the order of 1800 hr.

Dissolution of UO_2-PuO_2 Fuel Cores

It was previously reported that the Zircaloy-clad mixed PuO_2-UO_2 fuel elements for the Plutonium Recycle Test Reactor (PRTR) could be dissolved in a two-step procedure after decladding with ammonium fluoride–ammonium nitrate. In the first step, uranium dioxide is dissolved at 80°C with 15.5*M* nitric acid alone. In the second step, 0.1*M* fluoride is added to dissolve plutonium dioxide; this dissolution is also carried out[5] at 80°C. Currently, a preferred procedure[6] involves a similar decanning step, after which the fuel elements are subjected to a 2-hr treatment at 80°C with 11*M* nitric acid containing 0.1*M* fluoride. This is followed by a 30-min treatment at the boiling temperature with the same solution to which 0.3*M* aluminum nitrate has been added. Low-reactivity residues appear more amenable to treatment by this method.

Dissolution of plutonium dioxide in nitrate media is invariably more difficult than dissolution of uranium dioxide. Some of the factors affecting plutonium dioxide dissolution have recently been reported by Euratom workers.[7] Agitation, increases in nitric acid and fluoride concentrations, and increasing the temperature accelerate dissolution, whereas increases in the temperature of firing the plutonium dioxide retard its dissolution.

Ashing, Chlorination, and Extraction of Graphite-Based Carbide Fuels

Advanced gas-cooled reactor fuels, operating at very high temperatures, may contain thorium and uranium carbides coated with highly inert and refractory pyrolytic carbon and embedded in graphite. The Peach Bottom High-Temperature Gas-Cooled Reactor (HTGR) will use a fuel of this type. It is very difficult to recover the special nuclear material from such fuels, and complex operations such as grinding, burning, and leaching with corrosive reagents may be required.

Describing work conducted at Oak Ridge National Laboratory (ORNL), Gens[8] recently reported preliminary studies of a proposed process which may avoid some of the difficulties of procedures considered earlier for carbide-graphite fuels. In the new process the fuel will be burned and the ash chlorinated under relatively mild conditions to make it easily soluble in an aqueous solution suitable for solvent extraction. This will avoid both grinding (expected to be difficult to do remotely) and leaching with fuming nitric acid. Chlorination of the ash would be effected by carbon tetrachloride carried in nitrogen at 500 to 550°C. Subsequent dissolution would be accomplished in 6*N* hydrochloric acid. An Inconel vessel might be suitable for burning, chlorination, and dissolution. Extraction would then be carried out with diluted tributyl phosphate (TBP) in titanium equipment. The chloride content of the dissolved ash can be reduced if it is boiled down with hydrogen peroxide. A similar process for zirconium fuels was also described by Gens recently.[9]

Separations Processes

Much attention has been given to ruthenium chemistry over the entire period of development of solvent-extraction processes, since ruthenium is frequently the fission product that limits overall decontamination. Complexes of this element and the utility and stability of ion-exchange resins and other sorbents for heavy-element separations are discussed.

Ruthenium Decontamination in Extraction Processes

The nitrato complexes of nitrosylruthenium are the species principally responsible for dif-

ficulties encountered in the separation of ruthenium from uranium and plutonium in solvent-extraction processes based on nitrate systems. Trinitrato-nitrosylruthenium is readily extracted into TBP from dilute nitric acid solutions but may be reextracted from TBP by caustic or by stronger nitric acid. With repeated reuse of TBP solvents, ruthenium becomes impossible to remove completely by caustic washing. Since it was thought that slow formation of stable complexes with TBP degradation products might be concerned in this phenomenon, Wallace[10] at Savannah River recently attempted to prepare such complexes for study.

As an example, complex formation between trinitrato-nitrosylruthenium and dibutyl phosphoric acid (DBP) was attempted by stirring the substances together and holding at 70 to 120°C for 0.5 to 1 hr. The crude reaction mixture was dissolved in ether and was fractionated with caustic and hexane to yield oily and tarry materials of varying composition, although all contained phosphorus, nitrogen, and ruthenium. From the analyses, and on the assumption that a nitrosyl group remained in combination with ruthenium, the number of DBP groups per ruthenium atom varied from 1.5 to 3.2, whereas the number of nitrate groups was slightly less than 1 per ruthenium atom. Molecular weights in benzene varied from 465 to over 6000.

Somewhat similar products were obtained from nitrosylruthenium hydroxide and dibutyl phosphoric acid, from trinitrato-nitrosylruthenium with monobutyl phosphoric acid (MBP), and from dinitrato-nitrosylruthenium and DBP. The first of these had no nitrato groups, but 1.4 DBP groups were bound per ruthenium atom; the material was insoluble in caustic but soluble in hexane. The latter two were both soluble in caustic and had 2.2 and 0.8 phosphate groups, respectively, per atom of ruthenium.

All complexes and their fractions were soluble in 30% TBP in a hydrocarbon diluent. When such a solution of the ether-soluble nitrosylruthenium dibutyl phosphate complex was further diluted with the hydrocarbon diluent, a portion of the complex precipitated, carrying with it about one-third of the ruthenium activity originally present. This behavior is indicative of a mechanism of ruthenium retention by the solvent similar to that noted under process conditions.

The tendency of TBP solvents to extract ruthenium along with uranium adversely affects the decontamination performance of the extraction process. This difficulty may be minimized by adjusting the condition of the ruthenium in the process feed solution to minimize its extractability. In earlier work it had been attempted to remove ruthenium by volatilization as the tetroxide.[11] Lyon and Scargill at Harwell have recently described efforts to reduce ruthenium extractability by treatment of the feed solution with hydrogen peroxide or ozone.[12] They proposed to form inextractable tetravalent ruthenium species by oxidation of the nitrosylruthenium nitrato or nitro complexes which are present in the process solutions.

It is preferred to conduct the ozone oxidation at ambient temperatures to minimize the volatilization of ruthenium tetroxide, since such volatilization requires that the tetroxide subsequently be trapped or condensed. However, both with and without $10^{-3}M$ silver-ion catalyst, treatment of nitrosylruthenium solutions with ozone at 30°C does not result in much oxidation of nitrosylruthenium(III), and hence very little change in the amount of extractable species is observed. The oxidation, instead, tends to proceed to the undesirable tetroxide stage.

Somewhat more favorable results were obtained with hydrogen peroxide. However, the rate of decomposition of peroxide, although slow in $6M$ nitric acid, is very fast in the presence of nitrosylruthenium nitrato complexes. Treatment of the complexes with H_2O_2 in $3M$ nitric acid and $2.5M$ additional nitrate ion reduces the extractability of ruthenium. The decrease in distribution ratio corresponds to about 40% conversion of extractable to inextractable species and is not due to the formation of tetravalent ruthenium. More favorable results were obtained at higher acidity, and treatment with H_2O_2 in $8M$ nitric acid for 30 min decreased the ruthenium distribution ratio by a factor of 12. Continued treatment resulted in the formation of tetravalent ruthenium and an increase in the distribution ratio.

Ion-Exchange Separation of Highly Irradiated Plutonium from Transuranic Elements

Two steps of the transuranium-element recovery process described previously[13] have been carried out at ORNL on a pilot-plant scale. As described by Brooksbank and McDuf-

fee,[4] this work was undertaken to obtain significant quantities of the higher plutonium isotopes and to provide a transuranic–rare-earth concentrate for further process development. The feed material consisted of two lots of plutonium-aluminum alloy rods, totaling about 42 kg. One lot (24 rods) had been irradiated to about 87% burnup of ^{239}Pu; a second lot (8 rods) had been irradiated to 99% ^{239}Pu burnup. The slow dissolution of this alloy in nitric acid was described earlier in this Review.

Brooksbank and McDuffee also discuss the results obtained with the anion-exchange recovery and separation process for plutonium and transuranium elements. After the dissolver solution was treated with gelatin and filtered to remove silica, it was adjusted to 7*N* nitric acid concentration, and plutonium was sorbed from it at 60 to 70°C on 20- to 50-mesh Permutit SK resin in the first of two purification stages. Residual aluminum and fission products were scrubbed from the column with 7*N* nitric acid containing 0.11*M* fluoride, and the plutonium was eluted with 0.7*N* nitric acid. Ferrous sulfamate was used to assure the presence of tetravalent plutonium in the eluate. The solution was made up to 7*N* nitric acid and was then sorbed on a fresh column of Permutit SK resin. Overall recovery of plutonium in the final eluate was 93%, and its decontamination from fission products was effected by factors of 2 to 7×10^5. The plutonium from the 24-rod lot was 51% ^{240}Pu and 7% ^{242}Pu, whereas that from the more highly irradiated 8-rod lot was 15% ^{240}Pu and 75% ^{242}Pu.

Transuranium elements were recovered from the aluminum-bearing effluent from the first ion-exchange stage of the plutonium-purification process. The effluent was evaporated at its boiling point of 140°C for acid removal and concentration, then diluted to 2.5*M* aluminum, somewhat deficient in nitric acid, and filtered through sand to remove precipitated aluminum hydroxide. The latter was voluminous and difficult to wash and retained a significant portion of the transuranium elements. The transuranium elements, along with rare earths present, were absorbed from the filtrate by 50- to 100-mesh Dowex 1-X10 resin at 60 to 70°C. Residual aluminum and fission products, other than rare earths, were scrubbed from the bed with 8*M* lithium nitrate, and the rare-earth–transuranic concentrate was then eluted from the resin with 0.7*N* nitric acid. Overall recovery of the transuranic elements averaged 63%, and the transuranium-elements–aluminum separation factor was 70.

Severe radiation damage to the anion-exchange resins was apparent in both steps. In plutonium recovery a steady increase in plutonium loss and an increase in bed pressure drop were observed. The resin was replaced after an estimated dose of 4×10^8 rads. The spent resin was soft and black and had lost about one-third of its "salt splitting" capacity. Damage to the Dowex 1 resin used for transuranic-element recovery occurred at a higher rate, requiring renewal of the resin after each lot of feed had been processed.

Protactinium Chemistry

Protactinium-233 is an intermediate isotope occurring in the course of converting thorium to ^{233}U. Because of its 27-day half-life, its chemistry is of particular importance in the chemical processing of irradiated thorium in the thorium breeder cycle. A summary of recent advances in protactinium chemistry has been made available by the publication of the Proceedings of the Protactinium Chemistry Symposium[14] held at Gatlinburg, Tenn., April 1963. This conference included the work of U. K., German, and French workers and covered discussions of aqueous nitrate, sulfate, chloride, and perchlorate systems, along with fluoride salt behavior in dry systems.

Discussions of methods for protactinium recovery included consideration of peroxide precipitation, TBP extraction, and adsorption on unfired Vycor glass. The latter technique was noted some time ago in this Review.[15] Information on the method was covered in some detail in the Proceedings just referred to and has been brought up to date in a more recent report from ORNL by Moore.[16]

The unfired Vycor glass is a borosilicate and has many pores with diameters of about 4 mμ and a surface area of 150 to 200 m^2/g. It is used in the form of 60- to 80-mesh or 100- to 200-mesh powders loaded into an adsorption column. From a very dilute protactinium solution (0.05 g/liter), more than 99% was adsorbed from an 11*M* nitric acid feed solution (containing 0.5*M* thorium, 0.1*M* aluminum, and a small amount of fluoride) up to a column loading of 2 mg of protactinium per gram of glass. Greater than 99% was eluted

with 0.5*M* oxalic acid. From strong nitric acid, distribution coefficients of several thousand in favor of the glass can readily be obtained. Certain silica gels show similar behavior as adsorbers of protactinium. Since protactinium is intensely radioactive, its isolation prior to the processing of thorium for uranium recovery could be advantageous. (C. E. Stevenson)

Plant and Equipment Design and Operation

Dissolving Vessels

Bower et al. report[1,17] on several electrolytic dissolver runs made at the Idaho Chemical Processing Plant (ICPP) pilot plant. Data are presented for dissolution of simulated HTRE, APPR, PM3A, and Pathfinder reactor superheater tubes. Scale-up calculations indicate plant rates of 21 to 46 kg of uranium per day, and some preliminary design studies to convert the dissolver originally installed for Submarine Intermediate Reactor (SIR) fuel, which is constructed of Carpenter-20 alloy, to an electrolytic dissolver, are mentioned. This program has been reported in this Review several times,[18–21] and a topical report is to be issued soon.

Ray[22] reports on a possible improvement to the continuous dissolver for aluminum-uranium fuel [Materials Testing Reactor (MTR), Engineering Test Reactor (ETR), etc.] at the ICPP. The present dissolver consists of a long-tube (always-safe diameter) stainless-steel dissolver. The aluminum-uranium fuels are fed into the dissolver at the top on a semicontinuous basis. Nitric acid with mercuric nitrate catalyst is fed in at the bottom for a once-through pass, with dissolver product overflowing above the fuel rods.

It is proposed, and supported by the work reported, that a recirculation leg be added to this dissolver which would, by improving dissolving conditions, allow the catalyst concentration to be reduced by a factor of 3, thus saving approximately $50 per operating day (payout calculated at 45 days of operation).

Figure II-1 shows the flow sheet for the equipment used in pilot-plant runs. Aluminum rods were used in these tests as simulated fuel

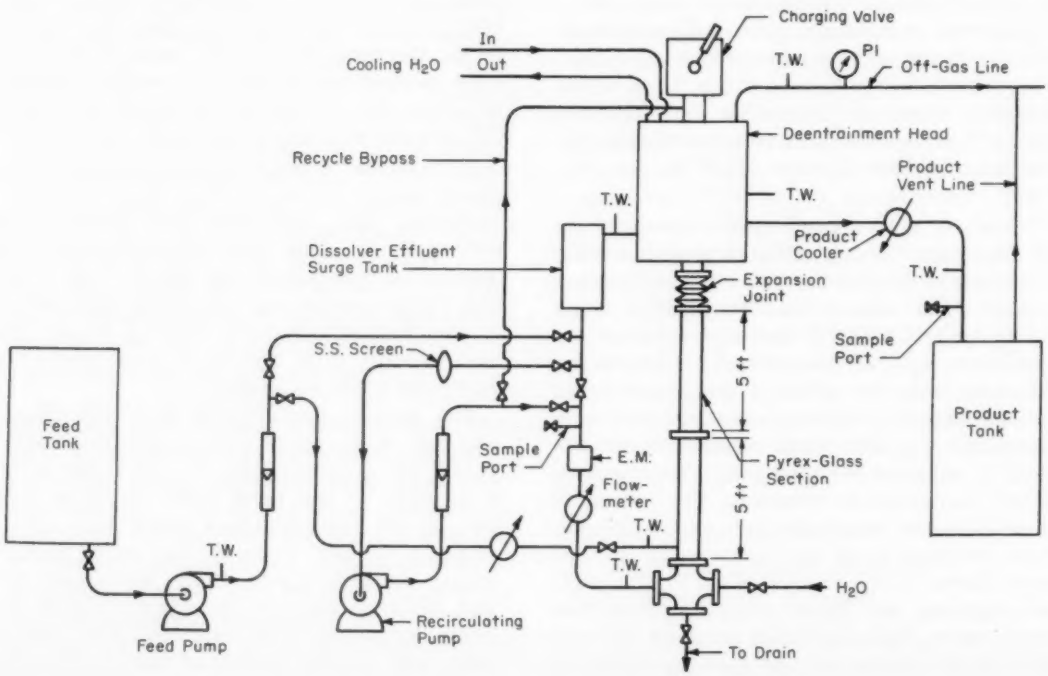


Fig. II-1 Flow sheet for pilot-plant recirculating dissolver.[22]

elements. These tests were made under four sets of conditions in dissolving aluminum rods:

1. *No recirculation* to obtain a base for comparison with the present plant operations.
2. *Forced recirculation,* which provided ideal conditions for study, but would be undesirable for plant operation since a pump would be required.
3. *Natural recirculation with acid feed added to the recycle line.* This gave wide flow fluctuations due to alternate violent and subsiding reactions, causing excess backpressure in the recycle line.
4. *Natural recirculation with acid feed added at the bottom of the dissolver.* This gave a much smoother operation and is the method recommended for plant modification.

Data are presented for several runs with various recirculation ratios (recirculation rate/feed rate). Figure II-2 shows a plot of some of the data. The reaction coefficient K_H is calculated from the empirical expression $K_H = (R_a / N^{0.95} m_f^{0.2})$ developed for previous dissolver runs.

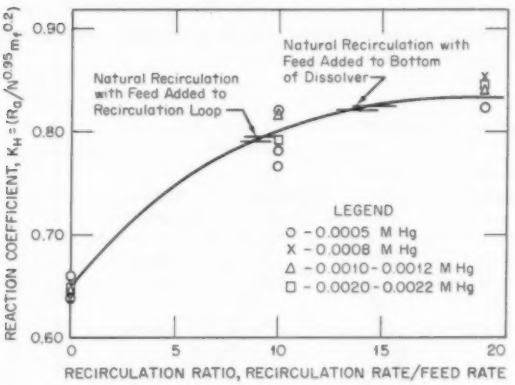


Fig. II-2 Effect of recirculation on reaction coefficient, K_H *(Ref. 22).*

K_H = reaction coefficient
R_a = aluminum dissolution rate, kg/day
N = nitric acid feed rate to dissolver, gram moles/hr
m_f = mercury concentration in feed, gram moles/liter

From the data in Fig. II-2, it was concluded that, for the same dissolution rate and acid feed rate, it would be possible to reduce the catalyst requirement by a factor of 3.2 by using natural recirculation instead of once-through operation.

Further data are also presented to show that, within standard deviations, the product is of equally uniform composition for either method of operation.

Critically Safe Solvent-Extraction Contactors

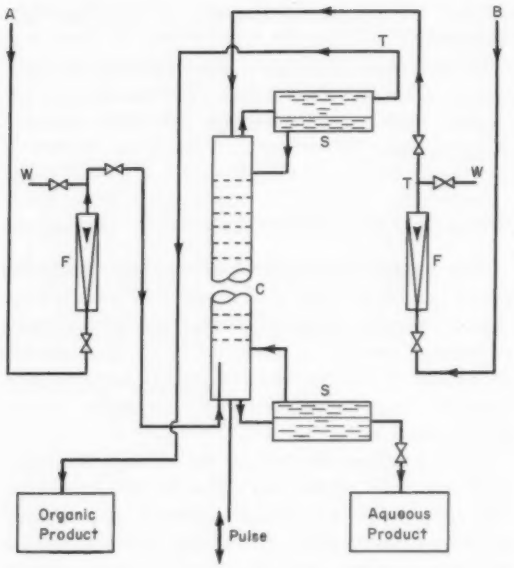
Two papers of interest covering high-throughput contactors originated from the United Kingdom. One by Logsdail and Larner[23] covers a rather complete study of high throughputs in pulsed plate columns for uranyl nitrate–20% tributyl phosphate/odorless kerosene–nitric acid systems.

A preliminary survey by the authors indicated to them that, of the two types of safe-by-shape contactors, pulsed plate columns and mixer-settlers, the former offered the greatest potential for high throughputs. They mention several means of increasing rates, namely, by increasing the plate hole size, the plate-free area, the plate spacing, or the phase density difference; by decreasing the continuous-phase viscosity; and by providing a surface on which the dispersed phase can coalesce. These increases are not unlimited, and in practice a compromise must be found between low mass-transfer efficiency of a spray column and the lower throughputs obtained in the pulsed columns when operated at their highest transfer efficiency.

This work was done to determine the maximum possible throughputs for a pulsed plate column. Figure II-3 shows the arrangement of equipment for all experiments. The column was 7.6-cm-diameter glass with a packed length of 305 cm. Figure II-4 shows a photograph of a typical nozzle plate used. The pulse was applied to the bottom of the column, via a stainless bellows, from reciprocating pumps to give a pulse amplitude up to 2.3 cm and a frequency between 40 and 200 cycles/min.

Table II-1 gives the characteristics of the plate cartridges used in the column, and Table II-2 gives the composition of the liquid-liquid system.

Three methods of approaching the flood point were considered: (1) Amplitude, frequency, and continuous-phase flow rate can be held constant and the dispersed-phase flow rate increased. (2) The amplitude and both phase flow rates can be held constant and the frequency increased to flooding. (3) The amplitude, frequency, and



A. Organic Feed
B. Aqueous Feed
C. Column
F. Flowmeter
S. Settler
T. Thermometer Pocket
W. Calibration Point

Fig. II-3 Arrangement of equipment.[23]

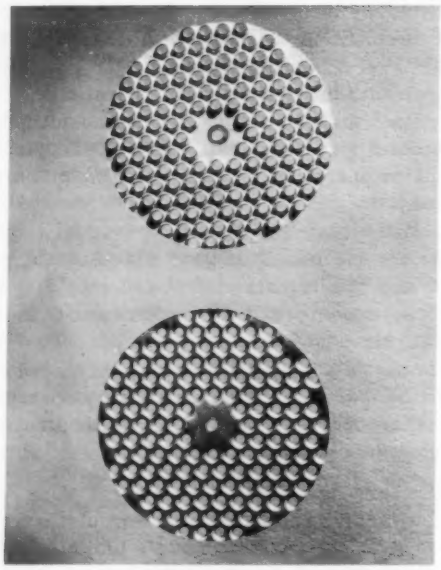


Fig. II-4 Nozzle plate.[23] *Top: lower surface of nozzle plate for aqueous phase dispersed. Bottom: upper surface of nozzle plate for aqueous phase dispersed (nozzles projecting downward).*

Table II-1 PLATE CHARACTERISTICS[23]

Cartridge	Plate material	Nozzle depth, cm	Nozzle* diameter, cm	Free area, %	Spacing, cm	Nozzle orientation
1	Stainless steel	0.102	0.30	23	5.1	Down
2	Stainless steel	0.102	0.30	23	5.1	Up
3	PTFE† coated stainless steel	0.102	0.30	23	5.1	Down
4	PTFE† coated stainless steel	0.102	0.30	23	10.2	Down
5	Stainless steel	0.102	0.45	33	5.1	Down
6	Stainless steel	0.102	0.45	33	10.2	Down

*All nozzles arranged on triangular pitch, height to half-base ratio 1.75.
†Polytetrafluoroethylene.

phase flow-rate ratio can be held constant and both phase flow rates increased to flooding. The third method was generally used, and flooding was considered to occur when the dispersed phase was rejected at its inlet. In general, the work was done with the aqueous phase dispersed.

For mass-transfer efficiency runs, samples were taken after the column had reached steady state (after at least four column-volume changes). The results are presented in many tables and curves.

MAXIMUM THROUGHPUT

Flood-point data are presented as the sum of the flow rate of both phases, V_c and V_d,* plotted against pulse frequency, f, which results in the curve having a maximum point that is termed the maximum throughput for the system. Figure II-5 shows a typical example of the work involving various cartridge designs. From these

*V_c = flow rate of continuous phase, liters/(hr)(cm^2); V_d = flow rate of dispersed phase, liters/(hr)(cm^2).

Table II-2 LIQUID-LIQUID SYSTEMS[22]

System	Organic phase	Aqueous phase	Phase dispersed
A, extraction	20% TBP/OK*	UN† + 3*N* HNO_3	Aqueous
B, scrub‡	UN + 20% TBP/OK	3*N* HNO_3	Aqueous
C, strip§	UN + 20% TBP/OK	0.01*N* HNO_3	Aqueous
D, strip§	UN + 20% TBP/OK	0.01*N* HNO_3	Organic
E, U-free	20% TBP/OK	0.01*N* HNO_3	Aqueous
F, U-free	20% TBP/OK	0.01*N* HNO_3	Organic

*Odorless kerosene.
†Uranyl nitrate.
‡*Scrub* is designated *strip* in the United Kingdom.
§*Strip* is designated *backwash* in the United Kingdom.

curves and others presented, it was concluded that the standard cartridge nozzle plate generally gave as high a throughput as any arrangement. Extraction and scrub systems generally showed maximum rates of 13 liters/(hr)(cm^2). For stripping, the rate was generally around 8 liters/(hr)(cm^2); thus the strip column was the limiting column for most systems. These figures compare favorably with a spray column having rates of 11 to 15 liters/(hr)(cm^2) and would scale up to 1 metric ton/day for a 15-cm-diameter column system.

MASS TRANSFER

Figure II-6 shows some of the data presented for height of transfer unit (HTU) values. This indicates a much smaller effect of frequency on extraction than on stripping. Other data indicated little effect on extraction with increase in flow rates, but strip HTU values can be increased by a factor of 3 when throughput is doubled.

OVERALL PERFORMANCE

The performance index is discussed to some extent as a means of comparing various systems. Performance index is defined as the ratio of the sum of the phase flow rates at flooding to the HTU. With this index, it was concluded that there is an optimum pulse frequency for each system, which does not necessarily coincide with the frequency for maximum throughput. The results also indicate uranium throughputs

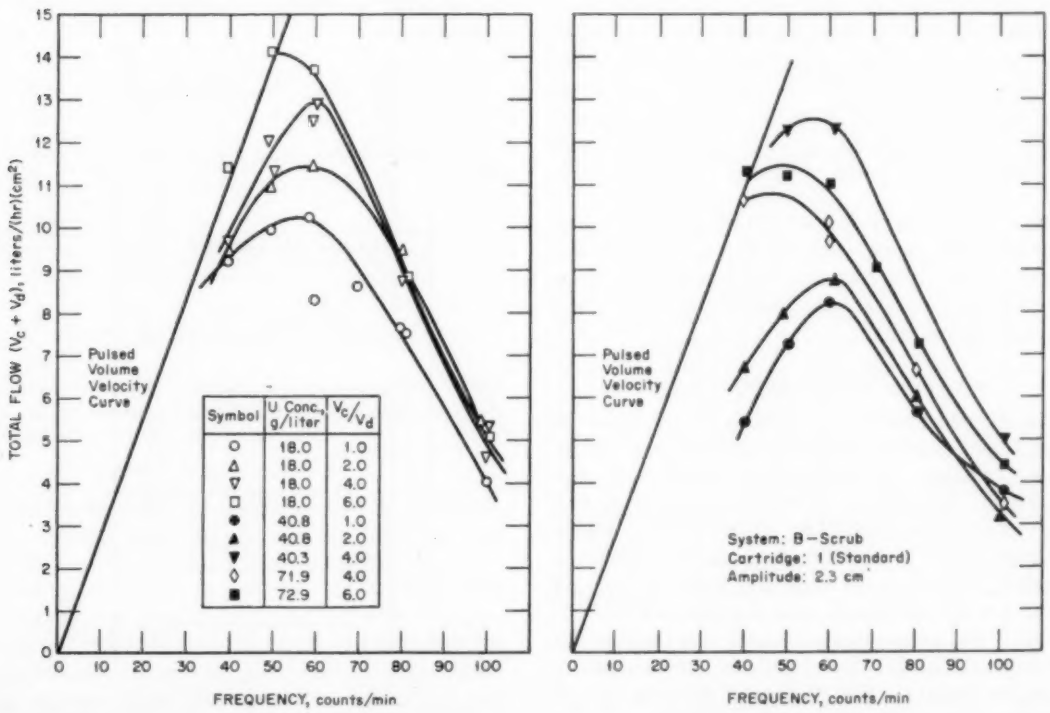


Fig. II-5 Total flow at flooding vs. frequency for scrub system.[23]

Symbol	System	Dispersed Phase	U Conc. in Feed, g/liter	Cartridge
○	C Strip	Aqueous	40-45	1 Standard
△	D Strip	Organic	14	1 Standard
◇	D Strip	Organic	65	2 Standard
●	A Extraction	Aqueous	100	1 Standard
▼	A Extraction	Aqueous	300	1 Standard

Amplitude: 2.3 cm
Flowrates: 80-90% Flooding

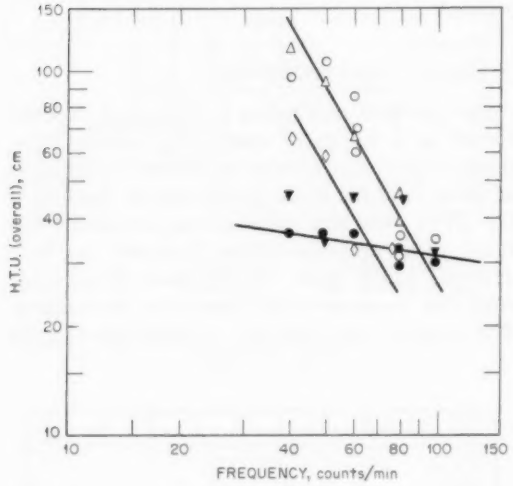


Fig. II-6 Comparison of effect of pulse frequency on HTU for extraction and strip systems.[23]

per unit volume of contactor to be several times better than those obtained for mixer-settlers with gravity settling. The authors go into some detail on drop size and nozzle size in relation to throughput data.

General Design of High-Capacity Mixer-Settlers

A second paper[24] is by Hanson and Kaye of the Department of Chemical Engineering, Bradford Institute of Technology. This paper describes the design and development of two prototype mixer-settlers of the safe-by-shape design for ^{235}U or ^{239}Pu processing. Assuming water reflection, Hanson and Kaye report 1.9 and 1.6 in. as infinite slab thicknesses for ^{235}U and ^{239}Pu, respectively. These are used as the basis of design. Two designs are described; one is vertical, Fig. II-7, and the other horizontal, Fig. II-8; prototypes of both have been built and run to prove the hydraulics.

The authors have developed a simple relation for the vertical design. Figure II-9 shows any two stages in the contactor. If it is assumed that the mixed-phase port is situated on the stage center line and that the densities of the phases do not change in flowing through these stages, then a pressure balance around the circuit *ABCD* shows that

$$\Delta P_{M(N)} + \Delta P_{H(N)} + \Delta P_{M(N+1)} + \Delta P_{L(N+1)} = (x-y)\rho_H + y\rho_L + x\rho_M - x\rho_L - x_M = (x-y)(\rho_H - \rho_L)$$

where ΔP_M, ΔP_H, and ΔP_L are the pressure drops through the mixed-, heavy-, and light-phase ports, respectively, of the stages indicated; ρ_M, ρ_H, and ρ_L are the densities of the mixed, heavy, and light phases, respectively. Flow in the counterclockwise direction was taken as positive. The right-hand side of the equation will always be positive, if no large density changes occur between the stages, confirming the existence of a positive driving force for flow in the direction shown. Similar equations apply for every pair of stages, the driving force being alternately clockwise and counterclockwise.

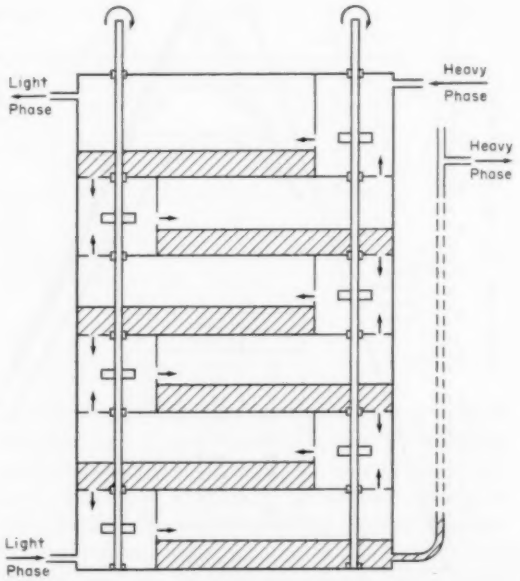


Fig. II-7 Flow pattern of two phases in vertical mixer-settler.[24] *(Reprinted with permission from* Chemical and Process Engineering.*)*

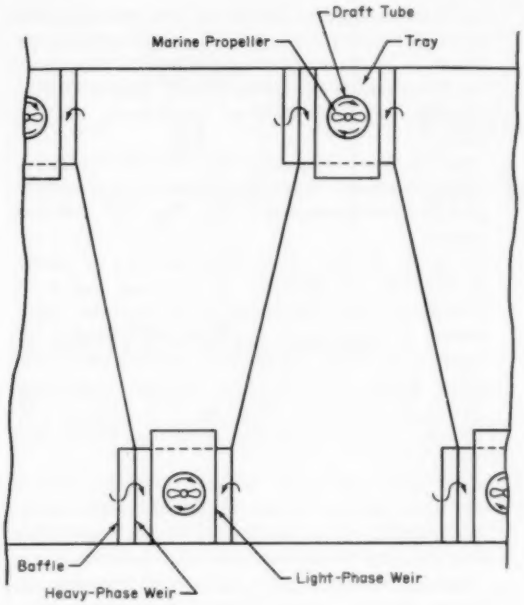


Fig. II-8 General plan of horizontal mixer-settler.[24] *(Reprinted with permission from* Chemical and Process Engineering.*)*

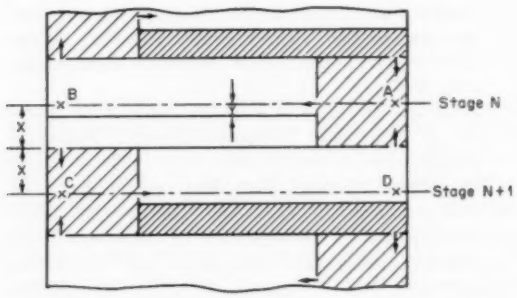


Fig. II-9 Hydraulic balance for two stages in vertical mixer-settler.[24] *(Reprinted with permission from* Chemical and Process Engineering.*)*

From the above equation it may be seen that the maximum driving force, and therefore the maximum flow rate, occurs when the interface level in the settlers and the mixed-phase port coincide and that the driving force can be increased for a given average stage height by sloping the floors of the settlers away from the mixer compartments. The latter has the advantage of increasing the depth of the settler near the aqueous and solvent ports, thereby aiding settling and minimizing the danger of backmixing.

Several runs were made in a prototype, three-stage 2-in.-thick unit with simple flat paddles for mixing and with means of varying the port sizes. Water and kerosene were used to study the flow patterns and pressure drops. For rates up to 150 gal/hr, discharge coefficients were within the range 0.65 to 0.85. It was determined that the interface could be controlled in the settling section by sizing the ports to the flows desired.

The second design employs the more conventional horizontal slab but overcomes the limitation on the driving force by mechanically lifting the mixed phase from the mixer compartments into the subsequent settling compartments. The general plan is shown in Fig. II-8, with details of the weirs and lifting arrangement in Fig. II-10.

The two phases flow by gravity over weirs from the settlers into the appropriate mixer compartments. Baffles in front of the heavy-phase weirs prevent the light phase from being carried over. A marine propeller drives the liquid out of the mixer compartment onto a tray. The liquid then flows by gravity into the settler. This arrangement provides a large capacity for transferring the liquid from the mixer to the settler compartments. Unlike other pumped mixer-settlers, the impeller speed does not need to be altered when the throughput is changed. Feeds may also be

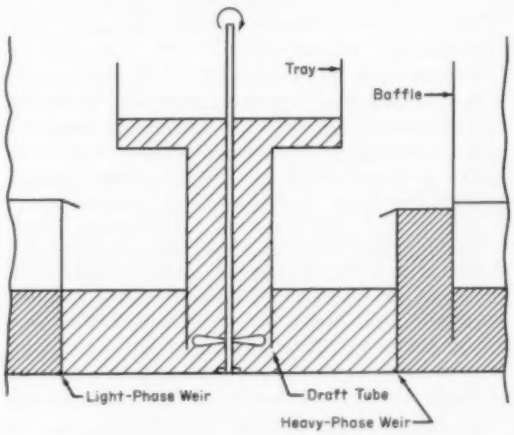


Fig. II-10 Weirs and lifting arrangement for horizontal mixer-settler.[24] *(Reprinted with permission from* Chemical and Process Engineering.*)*

introduced without difficulty at an intermediate stage. Because of the difference in levels between the mixer and settling compartments, the liquids flow freely over the weirs, making the different stages truly hydraulically independent. There is no possibility of any suction being applied to a settler compartment, and there can be no backmixing.

A one-stage model was built and operated with water to test the hydraulic characteristics, and curves are presented for effects of propeller position, cone angle in lifting device, propeller clearance, and viscosity.

The following conclusions are reported from this first set of results:

1. Optimum position for the propeller is just inside the draft tube. The propeller should be at the level at which it is desired to hold the liquid.

2. Propeller-to-tube clearance should be kept to a minimum.

3. Using a conical tube increased the efficiency somewhat.

4. Capacity was proportional to the density of the liquid, as expected, but increased viscosity had little effect except to increase the load on the motor. (D. M. Paige)

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Processes based on the volatility of uranium and plutonium hexafluorides have been proposed for the processing of various types of irradiated nuclear reactor fuels. Volatility processes are being applied to both highly enriched fuels and ceramic fuels of low enrichment. Since the concentration of uranium in enriched fuel is low, the initial step of the processing scheme involves the separation of uranium from the fuel matrix prior to recovery of uranium by volatility methods. For the recovery of uranium from alloy fuels, liquid-phase fused-salt volatility processes are also being developed. In these processes the fuel alloy is dissolved in a salt mixture to form uranium tetrafluoride, which is later converted to the volatile hexafluoride.

The American Institute of Chemical Engineers has published, in a recent issue of the *Symposium Series*, several articles devoted to the processing of nuclear reactor fuels by volatility techniques.[1] Included are papers devoted to fused-salt processes,[1b, 1e, 1g] the Nitrofluor process,[1f] the application of fluoride-volatility techniques to the processing of uranium dioxide fuels (Refs. 1*a*, 1*h*, 1j, and 1*k*), and descriptions of chlorination processes for both ceramic and alloy fuels.[1c, 1d, 1i] Most of these papers were presented at a symposium sponsored by the American Institute of Chemical Engineers in 1961 and were previously reviewed in *Reactor Fuel Processing*.[2]

Volatility Processes for High-Enriched Fuels

In the processing of reactor fuels containing highly enriched uranium, the initial step of the process involves the separation of uranium from the fuel matrix, thereby freeing the uranium for subsequent recovery by fluoride-volatility methods. Several processes that involve separation methods based on the relative volatility of chlorides are being developed. Studies are currently being made on zirconium-uranium and aluminum-uranium alloy fuels. Volatility processes are also being applied to graphite-matrix reactor fuels containing enriched uranium carbide.

URANIUM ALLOY FUELS

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium alloy fuels is being developed at Argonne National Laboratory (ANL).[3,4] Current studies are being made with uranium-zirconium and uranium-aluminum alloys. The process employs two principal steps in which chemical separation of the various fuel constituents is achieved by selective volatilization of chlorides and fluorides. The initial process step involves the separation of the alloying and cladding material (aluminum or zirconium) from uranium by reaction of the alloy fuel at 350°C with hydrogen chloride gas while the fuel is submerged in a fluid bed of inert particles. Separation occurs through the formation of the volatile chlorides of zirconium and aluminum, $ZrCl_4$ and $AlCl_3$. Uranium is converted to solid uranium trichloride during hydrochlorination and remains, for the most part, associated with the fluid-bed material. However, a portion of the uranium trichloride is entrained in the gas stream, and therefore a high-temperature gas filter is employed in series with the fluid-bed reactor to ensure adequate retention of uranium within the system. Recovery of uranium as uranium hexafluoride is achieved in the second step by the

reaction between uranium trichloride and fluorine at temperatures of 250 to 500°C. Treatment of uranium chloride with hydrogen fluoride prior to the introduction of fluorine is being considered in order to avoid the formation of chlorine trifluoride during fluorination of uranium chloride.

Process studies are being conducted in a bench-scale apparatus consisting of a $1\frac{1}{2}$-in.-diameter fluid-bed reactor and a $1\frac{1}{2}$-in.-diameter packed-bed filter. The primary aim of the bench-scale studies has been to establish conditions that would result in a minimal amount of unrecoverable uranium. Uranium losses are due primarily to: (1) passage of uranium through the packed-bed filter during the hydrochlorination step either as a volatile chloride or as a particulate solid and (2) retention of uranium by the alumina in the fluid bed and filter bed at the end of the reaction sequence. In recent tests, several processing parameters were evaluated with both zirconium-uranium and aluminum-uranium alloy fuels.[3] Uranium loss to the fluid-bed and filter-bed material after fluorination can be reduced to less than 1% of the uranium in the alloy charge by conducting the fluorination as follows: carrying out the reaction for 30 min at 250°C with an initial concentration of 5 to 10 vol.% fluorine in nitrogen, then raising the bed temperature to 500°C while gradually increasing the fluorine concentration, and fluorinating at 500°C with 90 vol.% fluorine for 2 hr to complete the reaction. With this two-temperature fluorination procedure, a residual concentration of < 0.01 wt.% uranium in the bed material was achieved (equivalent to less than 1% uranium loss). Residual uranium values in the case of aluminum fuels were generally lower than those obtained with Zircaloy alloy fuels. Sintered alumina, rather than fused alumina used previously,[5] appeared to be suitable as the fluid-bed and packed-bed filter material.

The depth of the alumina-bed material in the packed-bed filter affected the quantity of uranium lost during hydrochlorination. In the processing of uranium-aluminum fuels, an acceptable uranium loss of 0.1% of the uranium in the initial charge was obtained when the bed depth was greater than 9 in. A bed depth of only 6 in., however, was required for Zircaloy fuels.

The volatile chloride ($ZrCl_4$ or $AlCl_3$) produced during hydrochlorination of uranium alloy fuel represents a waste stream that requires processing for convenient storage. Studies at ANL[3] have shown that gaseous $ZrCl_4$ and $AlCl_3$ can be converted directly to solid oxides, ZrO_2 and Al_2O_3, by the gas-phase reaction with steam in a fluid-bed reactor. This process step allows the direct recovery and recycle of the HCl to the chlorination step after condensation of the excess steam used in the pyrohydrolysis reaction. Several tests were performed to simulate the recycle of moist HCl and to determine the effect of water at concentrations up to 1100 ppm in the inlet HCl on the hydrochlorination reaction. The presence of up to 1100 ppm moisture in hydrogen chloride did not appear to affect either the overall hydrochlorination rates or the hydrogen chloride utilization efficiencies. The presence of up to 20 vol.% hydrogen in the moist HCl stream did not appear to affect the hydrochlorination rate or efficiency.

A pilot-plant facility has been constructed at ANL to demonstrate the processing of up to 30-kg charges of uranium-zirconium or uranium-aluminum alloy in the form of multiplate assemblies.[3,4] A schematic diagram of the facility is shown in Fig. III-1. The facility consists of a 6-in.-diameter nickel fluid-bed reactor, a 9-in.-diameter packed-bed filter, a stainless-steel pyrohydrolysis reactor for conversion of volatile chlorides to oxides, cold traps for uranium hexafluoride, and equipment for disposal of gaseous reagents.

In tests performed with simulated alloy fuel elements (without uranium), average hydrochlorination rates of 3.0 kg/hr for zirconium alloy and 2.0 kg/hr for aluminum fuel can be readily achieved. By cooling the wall of the fluid-bed reactor with an air-water system controlled by a thermocouple located in the wall of the reactor, workers could maintain nearly isothermal conditions in the fluid-bed reactor, even during periods of high reaction rates.

From data obtained in preliminary tests in the pilot-plant facility, processing conditions for the hydrochlorination and hydrofluorination steps have been established (see Table III-1).[6] Data in Table III-1 are not considered optimum but represent the processing conditions which resulted in very satisfactory operation of the pilot-plant facility. The hydrochlorination temperatures are 50 to 100°C higher for Zircaloy alloy fuels, with the alumina-bed material maintained at 450°C for Zircaloy fuels and 350°C for aluminum fuels. Hydrogen chloride utiliza-

tion efficiencies of 50% or greater were obtained for batch charges of either fuel type without hydrogen chloride recycle.

A chloride-volatility process, based on the selective volatility of uranium hexachloride, is being developed on a laboratory scale for Materials Testing Reactor (MTR) type uranium-aluminum alloy fuels at Oak Ridge National Laboratory (ORNL).[7] The proposed process (Fig. III-2) involves chlorination of the alloy at 550°C in an open tube with a gas stream consisting of 5 vol.% CCl_4 in HCl. The addition of a small amount of CCl_4 to the HCl is required to convert the nonvolatile UCl_3 hydrochlorination product to higher valence uranium chloride compounds which are volatile. The aluminum in the alloy is converted to volatile aluminum trichloride. After the chlorination step is completed, the reaction vessel is cooled and washed with water to dissolve the nonvolatile chlorides of fission-product elements.

The volatile uranium chlorides are reduced to nonvolatile uranium trichloride in a separate vessel at 200°C with carbon monoxide. The aluminum trichloride is unaffected by its passage through the condenser and is collected as a waste stream. The uranium trichloride is partially decontaminated from condensed fission-product chlorides by purging with argon at 500°C. Uranium is recovered from the condenser as UCl_6 by reaction of UCl_3 with chlorine at 300°C. Alternative recovery steps that have been suggested are dissolution of the UCl_3 in cold water or fluorination of UCl_3 with fluorine at 200°C to form volatile UF_6.

On the basis of preliminary experiments and heat-transfer calculations, it appears that the chlorination reaction rate is limited to approximately 6 mils/hr, since at higher reaction rates the fuel-element temperature is expected to rise above the melting point of aluminum (650°C). At 6 mils/hr the 180-mil-thick side plates of the MTR element would be completely chlorinated in 15 hr.

Corrosion tests have shown that several nickel alloys such as A-nickel, Nichrome V, and INOR-8

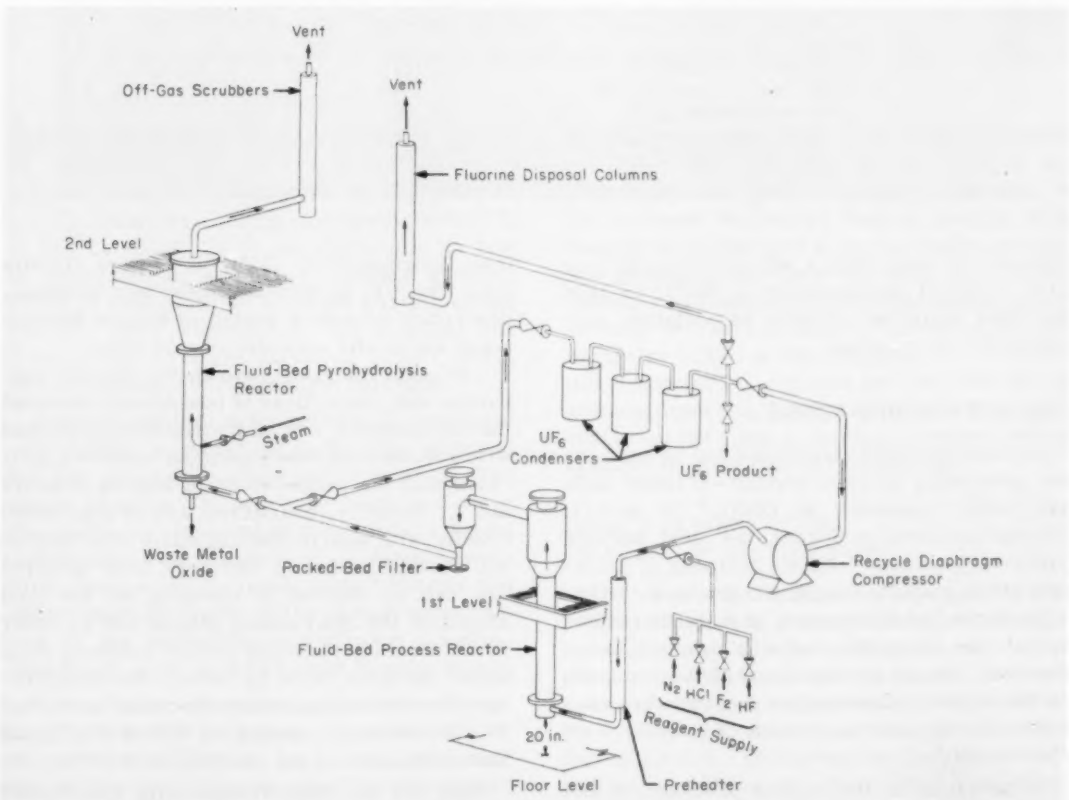


Fig. III-1 High-enrichment uranium-alloy volatility-processing pilot plant.[7]

Table III-1 PROCESSING CONDITIONS FOR PILOT-PLANT TESTS[6]

(Equipment: Main Reactor, 6-in.-Diameter Nickel Reactor Containing 40 Kg of Granular Alumina; Packed-Bed Filter, 9-in.-Diameter Unit Containing 9 Kg of Granular Alumina as Filter Medium; Pyrohydrolysis Reactor, 6-in.-Diameter Stainless-Steel Reactor Containing 20 Kg of Bed Material)

Processing parameters	Fuel material	
	Zircaloy fuel (PWR type)	Aluminum fuel (MTR and ETR types)
Hydrochlorination		
Typical charge		
Weight, kg	20	7
Number of plates	14	19
Length, in.	48	36
HCl concentration, vol.%	70	80
Gas velocity in reactor, ft/sec	0.6	0.6
Process temperatures, °C		
Reactor bed	450	350
Reactor wall	350	275
Packed-bed filter	350	200
Pyrohydrolyzer	350	300–350
Reaction rate, kg/hr	2.0–3.0	1.5–2.0
HCl utilization, %	50	60
Reaction time, hr	7–10	4–5
Inert-bed material		
Reactor bed	Alcoa T61 alumina, 28 to 100 mesh	
Packed-bed filter	Alcoa T61 alumina, 14 to 28 mesh	
Pyrohydrolyzer	Sand, 20 to 40 mesh	
Hydrofluorination		
HF concentration, vol.%	20	
Gas velocity in reactor, ft/sec	0.5	
Process temperatures, °C		
Reactor bed	350	
Packed-bed filter	350	
Reaction time, hr	2.0	

corrode at less than 1 mil/month in HCl or CCl_4 vapor at temperatures of 500°C or less and thus would be suitable as container materials for the process.

URANIUM CARBIDE FUELS

Engineering-scale investigations on methods for processing uranium carbide–graphite fuels are being conducted at ORNL.[8] Of several process concepts evaluated, the most suitable processing scheme consists basically of oxidation of the graphite matrix and uranium carbide with oxygen and fluorination of the oxide residue by fluorine to produce volatile uranium hexafluoride. Details of results of pilot-plant tests on the oxidation-fluorination process were presented in the previous issue of *Reactor Fuel Processing*.[9]

In the oxidation-fluorination process, the fuel is freed of graphite by burning in oxygen at 1000 to 1200°C. The oxide residue, or ash, is then fluorinated at 450°C to produce volatile UF_6. The UF_6 is decontaminated by a sorption-desorption step in a series of sodium fluoride traps and finally collected in cold traps.

Laboratory studies[8] have shown that the combustion ash, regardless of how densely sintered the ash might be, can be fluorinated rapidly and with greater than 99.8% uranium recovery, provided that the temperature is kept at or above 400°C. Powdery, unsintered ash is fluorinated readily with nearly 100% uranium recovery at 400°C. High uranium recovery from sintered ash can be effected by carrying out the final stages of the fluorination step at 530°C. Over 99.8% uranium recovery can be achieved from highly sintered oxide by using a two-temperature fluorination procedure (fluorination of about 95% of the oxide residue at 400 to 450°C and then completion of the reaction at 530°C).

Fuel for the High-Temperature Gas-Cooled Reactor (HTGR) is a dispersion of carbon-coated $(U\text{-}Th)C_2$ particles in a graphite matrix.

Gens[10] at ORNL is evaluating, on a laboratory scale, combustion-chlorination as a head-end step for uranium recovery by solvent extraction. Burning of the fuel is accomplished by reaction with oxygen at 800°C. Careful regulation of the fuel temperature during oxidation is necessary to avoid sintering of the oxide product. The oxide ash is converted to water-soluble chlorides by reaction with carbon tetrachloride vapor (15 vol.% CCl_4 in N_2) at 550°C. Chlorination is completed in 5 hr. Sintered oxide would require significantly longer chlorination periods or chlorination at higher temperatures to achieve complete conversion of the oxide to soluble chlorides. During chlorination with CCl_4 at 550°C, about 10% of the uranium in the fuel is converted to a volatile chloride species, which is condensed in a cooler portion of the reactor. After chlorination the uranium and thorium chlorides are dissolved at 20°C in 6*N* HCl containing 0.05*M* hydrogen peroxide.

A major problem in the process is associated with finding a suitable construction material for the combustion-chlorination reactor. The choice of materials is highly restricted since the reactor is also used as the container during dissolution of the chlorination products. Results from preliminary corrosion tests[10] indicate that the average corrosion rates of high-nickel alloys in the combustion-chlorination aqueous-dissolution cycle would be about 20 mils/month.

Bresee[11] has assembled a complete bibliography of reports pertaining to research at, or sponsored by, ORNL on Rover fuel-processing and molten-salt fluoride-volatility processes. Among the reports cited are topical reports describing development work on the processing of uranium from graphite-matrix fuel by oxidation-fluorination techniques.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

Several processes that involve separation methods based on the volatility of uranium hexafluoride and plutonium hexafluoride are being developed for the processing of uranium dioxide reactor fuel elements. A fluid-bed fluoride-volatility process is being developed at ANL[3,4] for the recovery of uranium and plutonium from spent uranium dioxide fuel. In the process the declad fuel is reacted with fluorine in a fluid bed to form volatile uranium and plutonium hexafluorides which are subsequently decontaminated and separated from one another. Workers at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium, are developing a fluorination process for the recovery of uranium from UO_2 fuel based on the initial conversion of the oxide to uranium tetrafluoride or uranium trioxide prior to fluorination.

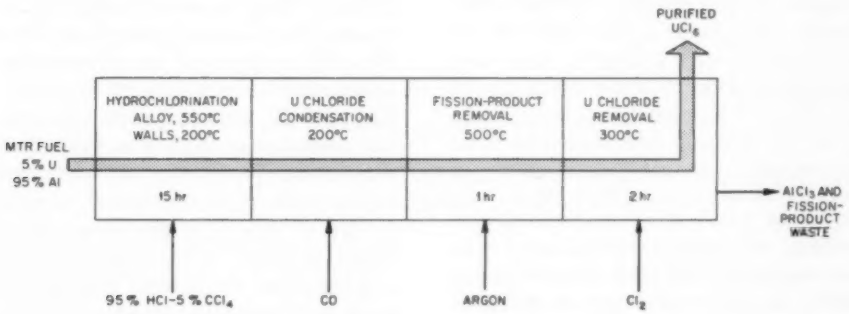


Fig. III-2 Preliminary flow sheet for hydrochlorination of uranium-aluminum alloy (MTR) fuel.[7]

DIRECT FLUORINATION OF URANIUM DIOXIDE FUEL

The direct fluorination of uranium dioxide pellet fuel is being studied at ANL[3] on an engineering scale in a 2-in.-diameter air-cooled reactor, using fused alumina as an inert-bed material. Current emphasis has been placed on the evaluation of a two-zone oxidation-fluorination scheme for conducting the fluorination reaction. In this scheme the lower (oxidation) zone of the reactor consists of a bed of declad uranium dioxide pellets with fused-alumina grain

filling the voids of the bed, and the upper (fluorination) zone consists of a fluidized bed of fused-alumina grain. Passing an oxygen-nitrogen mixture through the lower zone causes U_3O_8 fines to be produced and transported to the upper fluidization zone where the fines are fluorinated by fluorine to uranium hexafluoride.

In recent tests the two-zone oxidation-fluorination technique was evaluated for the processing of stainless-steel-clad pellets. Tests were performed with short lengths (1 in.) of stainless-steel tubing simulating sheared fuel elements and with longer element sections (10 and 12 in. long) in which the cladding had been slit or perforated longitudinally. Chopped, clad fuel rods were simulated by placing 0.42-in.-diameter by 0.42-in.-long cylindrical UO_2 pellets inside $^{15}/_{16}$-in. lengths of 304 stainless-steel tubing. The segments of tubing were placed in the reactor to form a 3-in.-deep fluidized-packed bed. Oxidation was carried out at 400 to 500°C with 88% oxygen in nitrogen. The fluorination was conducted with 3 to 14% fluorine at 500°C. Approximately 87% of the uranium charge was removed from the cladding in 12 hr; the remainder was removed by recycle fluorination at 500°C with 64 vol.% fluorine in nitrogen. In tests with longer clad segments, 10-in.-long pieces with a continuous longitudinal slit and 12-in.-long pieces with $^3/_{16}$-in.-long perforations spaced at $^{11}/_{32}$ in. intervals, uranium removal was complete in 9.5 and 7.5 hr, respectively. The perforated cladding (0.020 in. thick) was completely split open by the oxidation of UO_2 to U_3O_8. During the first 6 hr of the test, the fluorination rate averaged 30 lb of UF_6 per hour per square foot, and the fluorine utilization efficiency was 88%. On the basis of these demonstration tests, the two-zone technique appears to be effective both in removing UO_2 from slit and perforated stainless-steel tubing and in recovering the uranium as UF_6 with high fluorination efficiencies.

DECLADDING OF STAINLESS STEEL

Two alternative methods are being investigated for decladding of stainless-steel-clad UO_2 fuel elements: (1) oxidative decladding by reaction of UO_2 pellets with oxygen to produce U_3O_8, which forms as a very fine powder and readily separates from the cladding, and (2) the chemical destruction of the cladding by high-temperature reaction with oxygen in the presence of hydrogen fluoride.

Workers at ANL[3,4] have investigated the oxidative removal of uranium dioxide from stainless-steel cladding in a fluidized-packed-bed system. Separation of about 95% of the UO_2 from clad fuel segments was achieved in tests employing mechanical vibration of the fuel segments, pulsing of the fluidizing-gas stream, and a programmed temperature increase that allowed the initial stages of the oxidation to proceed at a slow rate.

Preliminary tests at ORNL[12] have shown that high oxidation rates for stainless steel can be obtained with gaseous mixtures of hydrogen fluoride in oxygen. Maximum reaction rates for 304L stainless steel occurred with gas compositions containing 40 vol.% HF. Oxidation rates of 67 mils/hr were obtained at 650°C. The reaction product was observed to be predominantly Fe_2O_3 with only 1% fluoride content.

The destructive oxidation of stainless steel by $HF-O_2$ mixtures has been investigated recently at ANL[13] in fluidized-bed equipment as a method for decladding UO_2 fuel elements. In tests performed in a 3-in.-diameter fluid-bed reactor, oxidation rates of approximately 30 mils/hr were obtained at 550°C for both 304 and 347 stainless steel with a reacting gas mixture containing 40 vol.% HF in oxygen with a fluidizing-gas velocity of 0.9 ft/sec. Granular alumina was used as the fluid-bed material. The sintered UO_2 pellets contained within the stainless-steel tubing (0.020-in. wall thickness) completely disintegrated during the 2-hr test. Oxidation rates obtained at 500°C were too low (approximately 1 mil/hr) to be of any practical significance. In an exploratory test performed in a $1^1/_2$-in.-diameter fluid-bed reactor, the rate of oxidation of 304 stainless steel was markedly higher for the portion of the rod immersed within the fluidized bed as compared with the section of rod exposed to the gas phase above the bed (Fig. III-3).

On the basis of these data,[13] it is expected that this decladding technique will be directly applicable to the fluoride-volatility process, since both the destructive oxidation of stainless steel and the direct fluorination of uranium oxide can be conducted in the same vessel. Preliminary corrosion data obtained at ORNL[12] indicate that Nickel 200 might be a suitable material of construction for $HF-O_2$ environments at temperatures up to 600°C; corrosion rates for Nickel 200 ranged from 0.1 to 0.4 mil/month.

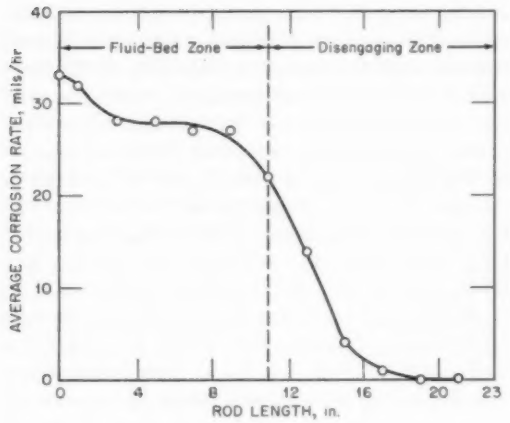


Fig. III-3 Corrosion rates at 550°C of type 304 stainless-steel rod immersed in a fluid-bed.[13] Initial dimensions, ½-in. in diameter and 23 in. in length; initial weight, 583.9 g; final weight, 392.4 g; run time, 3 hr; composition of feed gas, 40 vol.% HF, 40 vol.% O_2, and 20 vol.% N_2; fluidized-bed material, alumina.

VOLATILITY PROCESSES INVOLVING PRETREATMENT OF UO_2 FUEL

Workers at Centre d'Étude de l'Énergie Nucléaire, Mol, Belgium, are developing a fluorination process for the recovery of uranium from sintered uranium dioxide fuel.[14] Fluorine requirements are minimized by initially converting the oxide fuel to uranium tetrafluoride prior to fluorination to UF_6 with fluorine. The sintered oxide fuel is activated for hydrofluorination by oxidation with air to U_3O_8. A series of tests has been performed to evaluate the reactivity of U_3O_8-PuO_2 mixtures toward hydrogen fluoride at 450°C, producing a fluoride mixture containing PuF_4, UF_4, and UO_2F_2. It was observed that the rate of reaction of mixed oxide containing 3 to 10 wt.% PuO_2 with hydrogen fluoride is nearly identical to that obtained with pure, unsintered uranium dioxide. The rate of reaction of U_3O_8-PuO_2 mixtures containing 40% PuO_2 decreases markedly as compared with rates obtained with oxides containing low concentrations of PuO_2; a decrease in rate by a factor of $\frac{1}{300}$ was estimated.

All reactions in the process, $UO_2 \rightarrow U_3O_8 \rightarrow 2UO_2F_2 \cdot UF_4 \rightarrow UF_6$, are being studied in fluid-bed equipment.[14] Tests on the conversion of U_3O_8 to $2UO_2F_2 + UF_4$ have been carried out on a 3-kg scale. Approximately 3 kg of alumina served as an inert-bed material. It was observed that 95% conversion to fluoride can be achieved in 3 hr by reaction with 50% HF in N_2 at 350°C. Processing parameters for the oxidation of sintered UO_2 to produce finely divided U_3O_8 powder have been established in fluid-bed equipment using alumina granules as an inert-bed material. During the initial third of the reaction, the oxidation is carried out at 450°C with 50 vol.% oxygen in nitrogen. The oxidation reaction is completed at a temperature of 475°C, using a reacting gas mixture containing 20 vol.% oxygen. Under these conditions the total time to oxidize 3 kg of UO_2 is approximately 4 hr.

Preparation and Properties of Uranium Hexafluoride

REACTION OF CHLORINE TRIFLUORIDE WITH URANYL FLUORIDE

The reaction of chlorine trifluoride with uranyl fluoride to produce uranium hexafluoride is being studied at the Paducah Gaseous Diffusion Plant.[15,16] Reactions were carried out in the temperature range of 77 to 165°C and at pressures ranging from 28 to 42 mm Hg. In an effort to define the nature of the reaction, the gaseous reaction products were analyzed by gas chromatography.

The reaction between chlorine trifluoride and uranyl fluoride was observed to be essentially first order with respect to ClF_3 concentration. The activation energy for the reaction was calculated to be 8.9 kcal/mole. The mechanism of the reaction at the higher temperatures was postulated to occur stepwise:

$$2ClF_3 + UO_2F_2 \rightarrow ClO_2F + ClF + UF_6 \quad (1)$$

$$4ClF + UO_2F_2 \rightarrow O_2 + 2Cl_2 + UF_6 \quad (2)$$

$$ClO_2F \rightarrow ClF + O_2 \quad (3)$$

The overall reaction at completion is represented by the equation:

$$4ClF_3 + 3UO_2F_2 \rightarrow 3O_2 + 3UF_6 + 2Cl_2 \quad (4)$$

The reaction is complicated considerably by the secondary reactions involving ClF and ClO_2F. Chloryl fluoride decomposes at high temperatures to produce oxygen and chlorine monofluoride (Eq. 3). The rate of decomposition at 104°C is low, and therefore, at low temperatures, ClO_2F would appear as a reac-

tion product, as in Eq. 1. Chlorine monofluoride reacts readily with uranyl fluoride to produce uranium hexafluoride according to Eq. 2. The reactivity of ClF has been observed[15] to be between ClF_3 and F_2. The stoichiometry of the reaction of ClF_3 and UO_2F_2 will be between Eqs. 1 and 4, approaching Eq. 4 with long reaction times or higher temperatures.

CORROSION OF METALS BY URANIUM HEXAFLUORIDE

Langlois[17] has reported the results of an investigation on the corrosion of nickel alloys, gold, platinum, and stainless steel by uranium hexafluoride in the temperature range of 300 to 1000°C. Corrosion rates were estimated from changes in the electrical resistance of wire samples immersed in gaseous uranium hexafluoride. It was concluded from comparative tests that stainless steel, gold, platinum, and Inconel are corroded too rapidly to be suitable as container materials for UF_6 at temperatures above 500°C. At higher temperatures, only Monel and nickel appear to be suitable.

Dixmier and associates[18,19] have published descriptions of the techniques and apparatus that they used in studying the corrosion of metals by UF_6. The results of their study on the corrosion of iron and steel have been discussed in a previous issue of *Reactor Fuel Processing*.[20]

DISTILLATION OF URANIUM HEXAFLUORIDE

One method of separating volatile fluorides from uranium hexafluoride in fluoride-volatility processes is by distillation. In order to obtain information necessary for the design of distillation equipment, workers at ORNL are determining vapor-liquid equilibria for several fluoride systems.[12] In preliminary studies on the NbF_5-UF_6 system, it was observed that at 150°C the system exhibited a marked positive deviation from Raoult's law in the lower range of UF_6 concentration.

Shrewsberry and Musulin,[21] in a study of the VF_5-UF_6 system, have observed a negative deviation from Raoult's law at 75, 82, and 93°C. It is postulated that the negative deviations are indicative of the presence of strong intermolecular forces and perhaps the formation of a complex salt in the system.

Ivins at ANL[22] has investigated the separation efficiency of a 1½-in.-diameter packed column with the binary system UF_6-BrF_5. Several distillations were performed with the system methylcyclohexane and *n*-heptane for purposes of calibration. Flooding rates determined in the column packed with 1/16-in. nickel helices (single-turn wire rings) were 570 lb/(hr)(sq ft) for methylcyclohexane, 2680 lb/(hr)(sq ft) for UF_6, and 2200 lb/(hr)(sq ft) for BrF_5. The HTU_g was found* to be 1.2 in. for flows of 50 to 450 lb/(hr)(sq ft) for the *n*-heptane–methylcyclohexane system. The HTU_g for the UF_6-BrF_5 system was 1.3 in. at flow rates above 285 lb/(hr)(sq ft) and was found to increase to almost 3 in. at flow rates below this. In distillations performed with very low concentrations of BrF_5, the corrosion of the column and packing interfered with the separation performance as a result of the formation of BrF_3, which remained in the still pot. No azeotrope was found to exist in the UF_6-BrF_5 system.

(J. Barghusen)

Fused-Salt Volatility Process

Fluoride-volatility processes are being developed to provide an alternative to conventional aqueous processes for recovering uranium from spent nuclear fuels. The volatility techniques involve the conversion of uranium to the volatile hexafluoride (UF_6) as the principal means of separating it from fission products and fuel-alloy constituents. At ORNL a fused-salt volatility process has been under development for zirconium–uranium and aluminum–uranium alloy fuels. In this type of process, the alloy is dissolved in a molten fluoride salt with hydrogen fluoride sparging, and the UF_6 is obtained in a subsequent step with a fluorine sparge. The

*HTU_g is the height of a transfer unit based on the gas phase which is defined as

$$HTU_g = \frac{h}{NTU_g} = \frac{h}{\int_{y_1}^{y_2} \frac{dy}{y^* - y}}$$

where NTU_g = number of transfer units (based on vapor)
h = height of packed column
y^* = vapor composition in equilibrium with liquid
y_1, y_2 = mole fractions of component in vapor at entrance and exit

progress in the development of this process has been reviewed in previous issues of *Reactor Fuel Processing:* the zirconium alloy process was reviewed most recently in the Winter 1963–1964 issue, and the aluminum alloy, in the Spring 1964 issue. Subsequently, a summary report has appeared on the development of the aluminum alloy process.[23]

The present flow sheets for the aluminum-uranium alloy employ a $KF-ZrF_4-AlF_3$ salt system, which was selected on the basis of melting point, process capacity, salt cost, and dissolution rates of the aluminum alloy in the hydrofluorination step. In the course of this work, the phase-equilibrium diagram for the ternary system was determined; the phase diagram is shown in Fig. III-4.

Two alternative flow sheets are available for the aluminum-uranium alloy. The flow sheets, which have been referred to as the *step process* and the *recycle process*, are as follows:

Step process: (1) Dissolution of fuel in 60-40 mole % $KF-ZrF_4$ at 600°C until the following composition is attained: 51-34-15 mole % $KF-ZrF_4-AlF_3$ (neglecting UF_4 concentration); (2) addition of KF to change composition to 63.5-25.2-11.3 mole %; (3) dissolution of second batch of fuel until 51.5-20.5-28 mole % composition is reached; and (4) fluorination at 600°C to volatilize and recover UF_6.

Recycle process: (1) Dissolution of fuel in 67-21-12 mole % $KF-ZrF_4-AlF_3$ at 600°C until the following composition is reached: 51.8-16.2-32 mole %; and (2) fluorination at 600°C to volatilize and recover UF_6. Partial reuse of this waste salt with added KF and $2KF \cdot ZrF_4$ provides salt for a new dissolution cycle.

Other variants are possible; however, the basic requirement is to maintain salt compositions within the 600°C liquidus lines so that temperatures no higher than 600°C are entailed in the molten-salt process.

Dissolution rates for the step process ranged from 7 to 50 mils/hr at 600°C; no definite correlation with AlF_3 concentration was noted. Dissolution rates for the recycle process increased from 7 to over 40 mils/hr as the AlF_3 concentration increased from 12 to 35 mole %.

Volatilizations of greater than 99% of the uranium were obtained from the typical salt

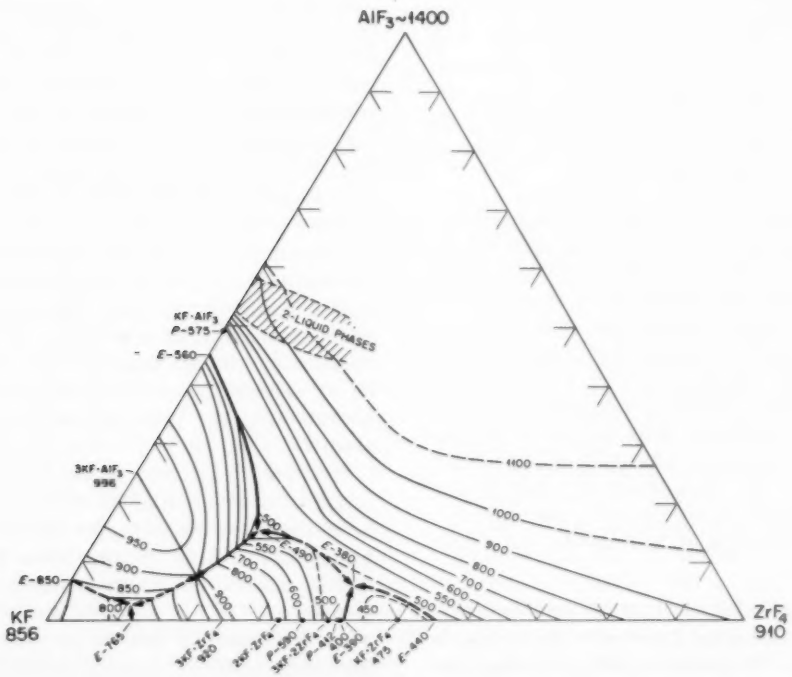


Fig. III-4 $KF-ZrF_4-AlF_3$ system.[23]

compositions given in the reference flow sheets at temperatures of about 600°C.

Other details of the process and a discussion of the mechanisms involved are also discussed in the ORNL report.

Bibliography of Fused-Salt Volatility Studies

A complete bibliography of molten-salt fluoride-volatility-process development and Rover fuel-processing studies at ORNL has been published.[11] The bibliography contains open literature references, topical reports, status and progress reports, and technical memoranda.

(W. J. Mecham)

Pyrometallurgical Processes

Pyrometallurgical processes are under development because it is believed that they may be advantageously employed in recycling fuels discharged from power reactors. Two important advantages of these processes are their ability to process short-cooled fuels, which makes possible minimum fuel inventories, and the avoidance or simplification of chemical conversions. Other advantages of these processes are the direct production of solid wastes, decrease in criticality problems because of the absence of aqueous solutions, and the retention of valuable fuel-alloying additives.

Pyrometallurgical processes are not high-decontamination processes, fission-product removals being just sufficient to maintain satisfactory nuclear and metallurgical properties of the fuel. The major processing objectives are repair of radiation damage and restoration of fuel reactivity. Because of the residual high-activity levels, remote refabrication of fuel elements is required. This is not a serious disadvantage because direct handling of extensively recycled fuel, even if highly decontaminated, would be precluded by the buildup of radioactive isotopes of fissionable and fertile materials.

D'Hont and Schmets,[24] at a symposium on Aqueous Reprocessing Chemistry for Irradiated Fuels held in Brussels in 1963, reviewed non-aqueous processing methods, including pyrometallurgical methods.

EBR-II Fuel-Cycle Facility

Constructed adjacent to the EBR-II reactor in Idaho, the EBR-II Fuel-Cycle Facility is a processing plant for the recovery and purification of discharged EBR-II fuel materials. Preparation of the facility for recovering the first fuel materials to be discharged from the EBR-II reactor is nearly complete.[4,25] Nearly all major equipment items are operable.[25] Progress in the installation and testing of various equipment items is discussed in recent progress reports issued by ANL.[25–27]

A recently issued research highlights report[4] of the Argonne Chemical Engineering Division includes an up-to-date description of the Fuel-Cycle Facility (see isometric sectional view in Fig. III-5) and the installed processing and refabrication equipment. Photographs in this report portray the sequence of processing and refabrication steps and the equipment for these steps. The processing and refabrication equipment are contained in two heavily shielded, interconnected cells, one with an air atmosphere (Air Cell), and the other with an argon atmosphere (Argon Cell).

Operations that do not involve exposure to the atmosphere of potentially pyrophoric materials (sodium and highly radioactive fuel materials) are conducted in the Air Cell. Typical operations include the disassembly of spent-fuel subassemblies for removal of clad fuel pins and the assembly of new subassemblies. Some of the installed processing equipment in the Air Cell is shown in Fig. III-6, a photograph of the interior of the Air Cell.

Operations that involve exposure of fuel materials and sodium to the atmosphere are conducted in the Argon Cell. Such operations include decanning of the fuel pins (Fig. III-7), purification of the fuel by melt refining (Fig. III-8), fabrication of new fuel pins (Fig. III-9), and cladding the pins and assembly of new fuel elements (Fig. III-10).

Nineteen 8-kg charges of unirradiated, chopped uranium-fissium fuel pins have been processed remotely in the melt-refining furnace.[4] The poured yields varied from 86.5 to 96.9%, most of the yields being about 95%. The ingots prepared in the melt-refining operation were subsequently used to prepare fuel pins by injection casting.[4] In this casting operation, molten fuel is forced by gas pressure into precision-bore Vycor (commercial silica) tube

molds. Both the melt-refining equipment and the injection equipment operated satisfactorily.

New reactor subassemblies are currently being prepared from unirradiated enriched EBR-II core alloy.[25] The core alloy was prepared by melt refining. Subsequently, about 350 fuel pins were produced from five batches of material processed in the injection-casting equipment.

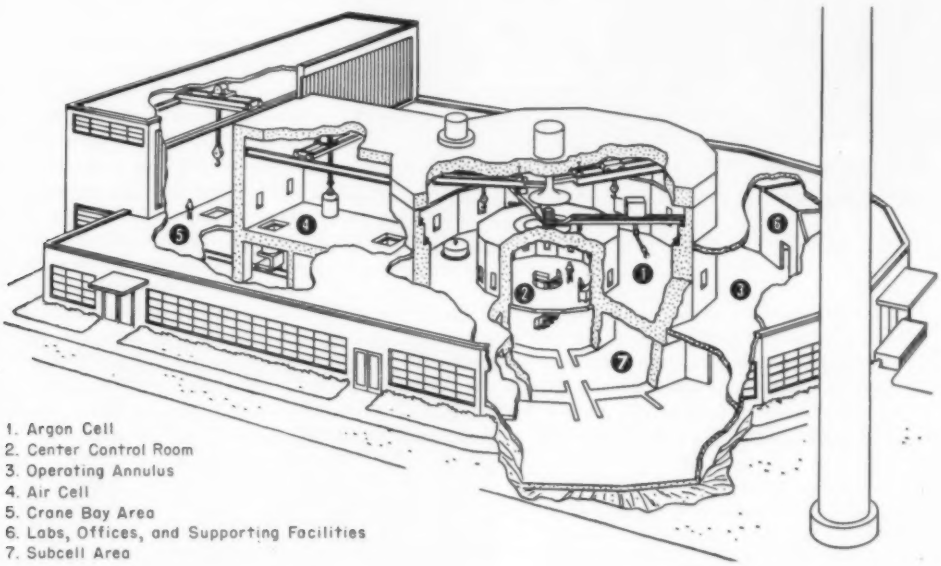


Fig. III-5 Isometric sectional view of the Fuel-Cycle Facility.[4]

The pins will be carried through the remaining fuel-refabrication steps and incorporated in new reactor subassemblies.

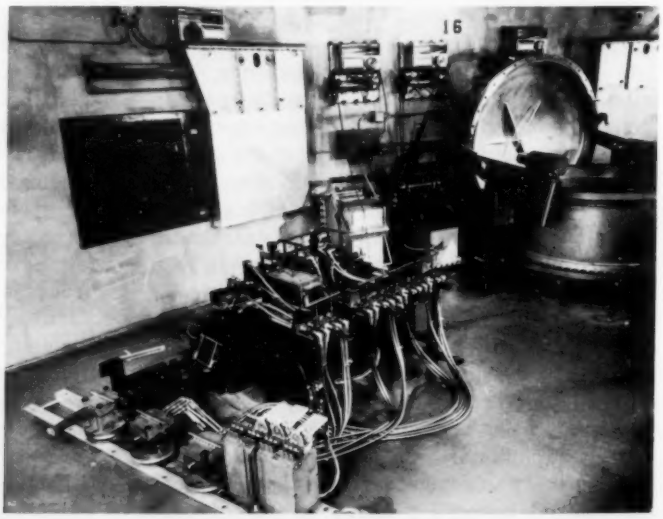
In August 1963 an argon atmosphere was[28] initially established in the Argon Cell, which has a volume of 65,000 cu ft. After a period of satisfactory operation in which very low oxygen and water concentrations were maintained (45 and 2.5 ppm, respectively),[29] the efficiency of the purification system began to decrease.[30] This resulted from a reduction of the activity of a catalyst bed where oxygen is catalytically combined with hydrogen to give water, which is subsequently removed on a Molecular Sieve dryer. The reduced catalyst activity was attributed to poisoning by mercury[31] which had previously been blown into the cell from a seal on a roof blister.[29] In February the argon atmosphere was replaced with air, and personnel entered the cell to clean up the mercury and do other corrective work.[31] At the same time the poisoned catalyst was replaced by fresh catalyst. In late February an argon atmosphere was reinstituted in the cell, and since that time the water concentration has been maintained below 50 ppm and the oxygen concentration at about 5 ppm.[25,27] A very low inleakage rate of 0.005 scfm has been achieved.[27]

The low inleakage rate and the maintenance of low oxygen and water concentrations in the large volume of argon gas are considered notable achievements.

Nitrogen is not removed from the argon atmosphere of the EBR-II Argon Cell, and its concentration is expected to be about 5%, depending upon the air inleakage rate and the rate of replacement of the cell gas with high-purity argon. Although nitrogen concentrations of a few percent may be tolerated for the initial processes to be employed in the Fuel-Cycle Facility,[32] the removal of nitrogen from argon by gettering the nitrogen on hot (~900°C) titanium sponge is under study because such removal may be necessary for future processes and fuels which may be studied in the EBR-II complex.[26,32] The kinetics of the nitrogen–titanium sponge reaction is being studied,[32] and a pilot plant (see Fig. III-11) has been con-

Fig. III-6 Air Cell and process equipment.[4] The Air Cell will be used to disassemble partially spent EBR-II fuel subassemblies and to test refabricated fuel elements and to assemble them into subassemblies for return to the EBR-II reactor. The spent EBR-II fuel subassembly will be transported in an interbuilding fuel coffin from the EBR-II reactor. The subassembly will then be removed from the interbuilding coffin and brought into the Air Cell through an opening in the cell floor (not visible here) and will be placed in the dismantler, seen along the left wall, where the subassembly will be disassembled. Sodium-bonding equipment and testing equipment for refabricated fuel elements are shown along the right wall. Temporary storage of spent and refabricated subassemblies will be provided by 10-ft-deep storage pits covered by the disks seen in the center foreground. The small transfer locks are in the background (mounted horizontally in the shielding wall between the Air Cell and the Argon Cell). A machine for assembling refabricated fuel elements into subassemblies is to be installed.

Fig. III-7 Argon-Cell transfer locks and fuel-element-decanning (and pin-chopping) equipment.[4] Transfer of materials between the Air Cell and the Argon Cell will be made through either a large transfer lock (right background) or two small transfer locks (center background). After an EBR-II fuel subassembly has been disassembled in the subassembly dismantler in the Air Cell, the fuel elements will be transferred to the Argon Cell through the small locks. The fuel elements will be placed in the spiral decanner and pin chopper (foreground), where the stainless-steel jackets will be removed and the uranium fuel pins cut to proper length for use in the melt-refining furnace.



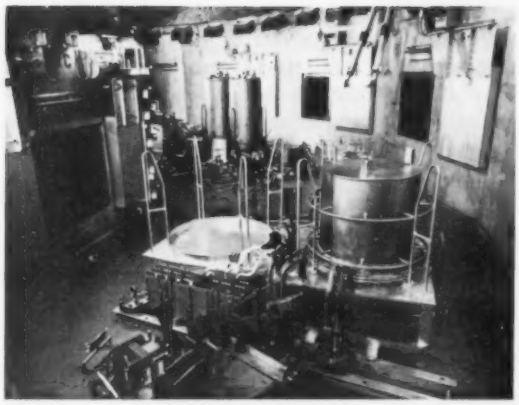


Fig. III-8 Argon-Cell melt-refining and pin-casting equipment.[4] The chopped fuel pins will be moved from the spiral decanner (and pin chopper) and charged into a melt-refining furnace (under the metal bell jar seen in the center foreground), where the pins will be melt refined, after which the purified molten uranium will be poured into a graphite mold. The refined ingot will be removed from the mold by means of an ingot remover and sampler (left foreground). The ingot will then be transferred to an injection-casting furnace (the tall metal bell jar seen in the center background) for melting and casting into fuel pins. The melting and casting into pins will be carried out by pressurizing the furnace to force the molten uranium into Vycor-glass mold tubes. A bank of service feedthroughs is seen at floor level between the melt-refining furnace and the ingot remover and sampler. Steel shutters to protect the windows from radiation damage when the windows are not in use are seen hanging from the window-shutter rails above the shielding windows.

Fig. III-9 Argon-Cell fuel-pin-processing equipment.[4] The pins will be moved from the injection-casting furnace (the tall metal bell jar in the center foreground) to pin-processing machines (foreground), where the following operations will be carried out: the Vycor-glass mold material will be removed from the pins and the fuel pins will be cut to length and inspected for diameter, length, weight, and porosity. The melt-refining furnace is seen in the background.

Fig. III-10 Argon-Cell fuel-element-assembly station and fuel-element-welding equipment.[4] The fuel pins will be moved from the pin-processing machine to the fuel-element-assembly table (right background), where they will be placed in stainless-steel cans containing the proper weight of bonding sodium. The assembled elements in a magazine (20-pin capacity) will be transferred to a settler (seen at notched corner of assembly table), where the fuel elements will be heated to distribute the sodium inside the assembled elements. After the sodium has melted, the restrainer plugs will be added. The assembled elements in a magazine will then be transferred to the welding machine, where a gas-tight closure of the stainless-steel can will be made. The magazine will be placed over the pedestal in the welding machine, and one element at a time will be welded. The welding machine, with a loaded magazine in front of it, is in the center foreground.

structed to obtain information on the reliability of components of a nitrogen-removal unit.[26,32] As shown by Fig. III-11, the direction of gas flow through the titanium sponge bed is periodically reversed by means of a four-way valve in order to alternately recover and store heat in the regenerative heat exchangers. The gas, which contains between 50 and 50,000 ppm nitrogen, is circulated at a rate of near 10 cfm.

The pilot plant has been operated continuously for 1000 hr.[26] All components and instrumentation performed their design functions well. During this long-term reliability run, the system successfully demonstrated the feasibility of large-scale removal of nitrogen from argon by hot titanium sponge.

Operation of equipment, particularly equipwith electric brushes and bearings, in a dry argon atmosphere has created a number of problems which arise largely from loss of lubricity.[4] For this reason a program has been instituted at ANL[25] for testing in a high-purity argon atmosphere equipment items destined for use in the EBR-II Argon Cell.

Melt-Refining Technology

In the melt-refining process to be used for recovery of the first EBR-II core material, over 99% of the iodine is removed from the fuel by vaporization.[33,34] In preliminary small-scale studies, this iodine was[34] collected primarily as CsI.

An iodine tracer experiment has been made with equipment in the Argon Cell of the Fuel-Cycle Facility to determine the fate of iodine in this equipment and, in particular, the efficiency of equipment for removing iodine from furnace off-gases.[25,27] One curie of ^{131}I was charged to a melt-refining crucible as palladium iodide in a glass capsule along with chopped uranium-fissium pins. The crucible was covered with a Fiberfrax fume trap (an inverted cup consisting of molded alumina-silica fibers previously coated with sodium to simulate the bonding sodium which is volatilized from spent fuel); the charge was heated to 1400°C, liquated at this temperature for 3 hr, and then cast into an ingot.

The disposition of the iodine, which was about that expected, was as follows:

Component	Iodine charged, %
Fume trap	81
Bell jar and base plate	23
Crucible plus skull	2
Ingot	7×10^{-3}

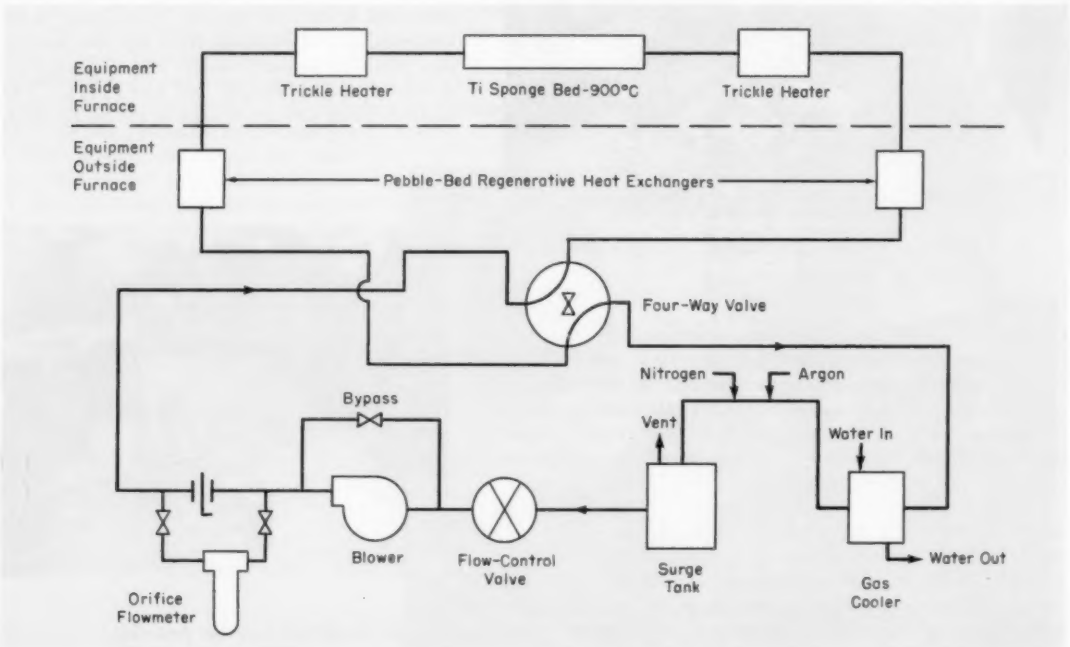


Fig. III-11 Schematic diagram of pilot-plant equipment for removal of nitrogen from argon.[4]

Most of the iodine was deposited in the fume trap, and substantially all of it was retained within the furnace.[25]

The in-cell filter in the off-gas line removed approximately 99.5% of the activity that reached it. About 93% of the iodine that passed through the in-cell filter and reached the vacuum pump (located in the subcell) was retained in the pump oil. No iodine was detected in the gas discharged to the off-gas delay tank.

After the melt-refining step, the skull was oxidized, and it was found that all of the iodine originally in the skull remained in the skull oxide.

The melt-refined ingots were used to produce pins by injection casting. These and the residual metal heel had about the same concentration of iodine as the melt-refined ingot. About 1.5% of the iodine from the ingot was found in the oil of the injection-casting furnace vacuum pump.

These iodine results are reassuring and substantiate previous conclusions[35] that iodine will not pose a serious problem in the handling of furnace off-gases in the Fuel-Cycle Facility.

General Information

A new book entitled *Uranium* has been published by Gittus.[36] The book contains information on the preparation of uranium metal from ore, fabrication, physical properties, deformation and preferred orientation, recovery, recrystallization and grain growth, mechanical properties, effects of irradiation and thermal cycling, and corrosion. It also includes binary- and ternary-phase diagrams for important uranium alloys, along with the physical properties and diffusion data for the alloys.

Electron-beam systems for melting and purifying refractory and reactive metals have been described by Wood and coworkers of the Bureau of Mines.[37] They have constructed two electron-beam furnaces that operate on the principle of high-powered vacuum diodes. The evolution of impurities at thousands of liters per minute at 10^{-5} torr with tens of kilowatts of power at 5 to 10 volts has been achieved. Small ingots weighing several kilograms have been produced by feeding the charge material as a consumable electrode. Appreciable purification of hafnium has been achieved in these furnaces.

Development of Liquid-Metal and Salt Processes

Several pyrometallurgical processes are based on separations that can be achieved in molten-metal and molten-salt solvent media. Separations are achieved by selective precipitation of certain elements and by selective oxidation or reduction reactions and subsequent selective transfer of the oxidized or reduced species between phases.

EBR-II Skull Reclamation Process

The methods mentioned above are utilized for separating impurities from uranium in a process under development at ANL. This is the skull reclamation process for the recovery and purification of melt-refining crucible residues (known as *skull material*). The crucible residue is first oxidized to convert it to an easily poured oxide powder. This powder is subsequently suspended in a halide salt, after which a series of steps involving transfer of solute elements between molten zinc-magnesium and halide salt phases and selective precipitations in metal phases is performed. After each step an impurity-bearing salt or metal phase is separated as completely as possible from an uranium-bearing phase. Finally, uranium is isolated from a zinc-magnesium solution by vaporizing the solvent metals and is consolidated by melting. This process was described in a previous Review.[38]

Progress made in the development of this process has recently been summarized in a research highlights report of the Argonne Chemical Engineering Division.[4] The five process steps involving liquid-metal and salt phases and intervening between the first and the last steps (skull oxidation and retorting) are conducted in a single crucible within a bell-jar furnace (Fig. III-12). A tungsten crucible, used to contain the highly corrosive liquid-metal and salt phases, is centrally located within a 24-in.-OD by 32-in.-high bell jar. Enclosure of the furnace within a bell jar allows an argon atmosphere to be maintained in the system and permits pressurization of the furnace for transfer of molten metals or salts through a pipe to a waste container, or, in the case of the uranium-product solution, to a retorting crucible. Two bell-jar furnaces are available, both of which are located in an open glove box. Eventually the glove box will be closed, and an inert argon at-

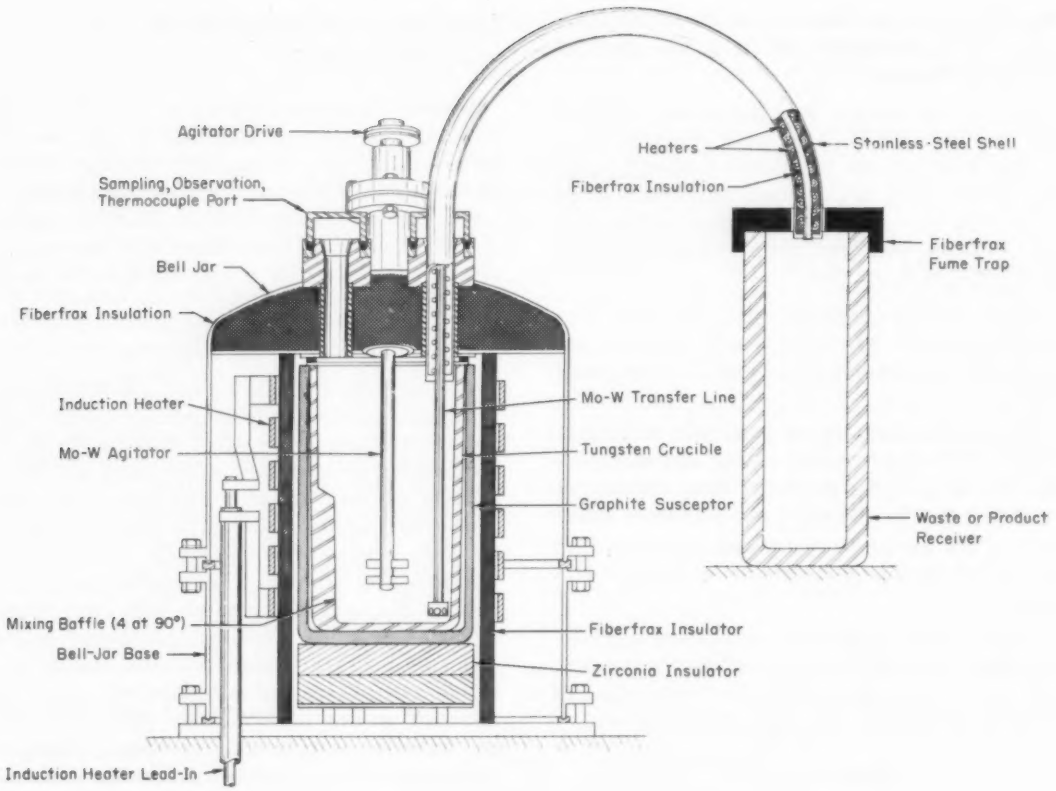


Fig. III-12 Bell-jar furnace for skull reclamation process.[4]

mosphere will be maintained within it to duplicate conditions in the EBR-II Fuel-Cycle Facility.

Eight runs have been performed to date on a 1.5-kg uranium scale in the skull-reclamation-process pilot plant in order to develop reliable operating procedures and to improve equipment performance.[4] The major operations (mixing, phase separations, and sampling) have, in general, been satisfactorily accomplished, but difficulties have been experienced with the solution transfer line (heater failures and line plugging). Preliminary chemical results show process performance (uranium recovery and fission-product removal) to be adequate, with the exception that removal of noble metals has been low. This was attributed to insufficient mixing in the noble-metal extraction step, a hypothesis that has been partially confirmed by more recent work.[27] Various items of information related to the flow sheet and to process and equipment performance are contained in three recent progress reports[25–27] from ANL. The performance of various candidate materials of construction for use in the skull reclamation process has recently been summarized.[4]

In the final step of the skull reclamation process, a zinc–12 wt.% magnesium–10 to 12 wt.% uranium-product solution will be retorted to distill the solvent metals and to consolidate the uranium by melting. Design features of (1) a recently constructed plant-scale distillation unit capable of handling a 36-kg batch of product solution (see Fig. III-13) and (2) a smaller 3-kg apparatus of the same design have recently been discussed.[4] Six runs have been made in the small equipment, the same BeO crucible having been used in all six runs.[25,27] Very high recoveries of the uranium (95 to 99%) as a consolidated metal button weighing about 300 g have been achieved. A small amount of black powder, identified as uranium hydride, has also been present with the product.[27] Traces of moisture present in the

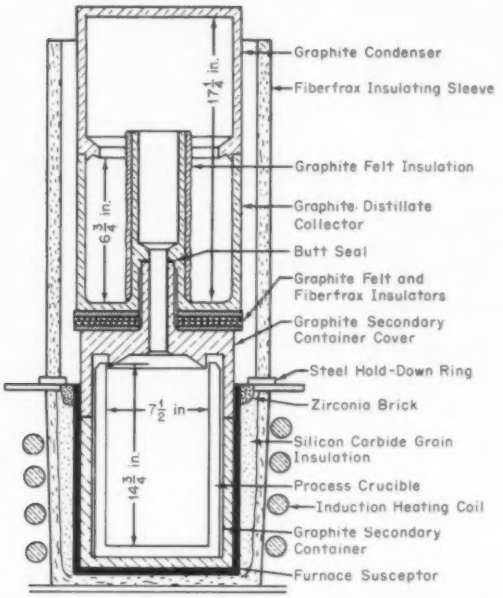


Fig. III-13 Magnesium-zinc distillation apparatus[4] (36-kg scale).

furnace are believed to constitute the source of hydrogen.

EBR-II Blanket Process

A blanket process, the major objective of which is to concentrate plutonium from 1 wt.% (its approximate concentration in discharged EBR-II blanket material) to at least 40 wt.% in uranium, has been previously described in these Reviews.[39] Except for final concentration of a dilute plutonium-product solution, this process has been fairly well demonstrated (500-g uranium scale). Some work on the product concentration step has been reported.[4] Solutions of 50 wt.% magnesium–zinc containing cerium or tin as a stand-in for plutonium have been concentrated by evaporation. The major conclusion for this work is that reflux of condensed metal vapors must be induced within the still pot in order to dissolve and wash back into the still-pot liquid any solute (e.g., plutonium) which may be deposited on the wall.

Advanced Processes for Plutonium-Containing Fuels

Pyrometallurgical processes are under development for plutonium-bearing fuels of the various types (metals, carbides, or oxides) which are being considered for use in fast power-breeder reactors. Because insufficient information is available on specific fuel compositions and cladding materials, the development effort has been focused on basic separations that would be common to a variety of flow sheets. In effect, rare-earth and noble-metal fission products are separated from plutonium and uranium by selective oxidation and reduction reactions. Perhaps the most unique feature of the process shown in Fig. III-14 is the rare-earth extraction step, in which rare-earth elements are preferentially distributed to the salt phase and uranium and plutonium to the metal phase according to reactions of the following type:

$$M(\text{metal}) + \frac{x}{2}\,MgCl_2(\text{salt}) \rightleftharpoons MCl_x(\text{salt}) + \frac{x}{2}\,Mg(\text{metal})$$

Distribution coefficients of uranium, plutonium, and various rare-earth elements between $MgCl_2$ and zinc-magnesium phases were presented in a previous Review.[40] Four to six extraction stages are required in order to provide adequate separation of rare earths from plutonium and uranium.

Consideration is now being given to the use of ternary metal systems of zinc, magnesium, and cadmium containing a high proportion of cadmium (Refs. 4, 25, 26, and 28). A conceptual process for a metallic fuel is shown[4] in Fig. III-14. The ternary system appears attractive because low operating temperatures (500 to 600°C) and low zinc concentrations may permit the use of series 400 stainless steels instead of tungsten or tantalum for process vessels. One of the principal criteria governing the choice of the metal-phase composition is adequate solubility of uranium and plutonium. In Fig. III-15, the solubility of uranium is shown as a function of composition of the metal phase.[4] Two regions of high uranium solubility are evident, one at about 50 at.% zinc–50 at.% magnesium and another at 83 at.% cadmium–17 at.% zinc. The latter region, which has the greater uranium solubility and the lower rate of corrosion of stainless steels, is favored.

The presence of plutonium as a plutonium-to-uranium ratio of 1 to 4 in a 69 at.% cadmium–16 at.% zinc–15 at.% magnesium solvent did not affect the uranium solubility over the range[25] of 390 to 690°C, and the plutonium solution was

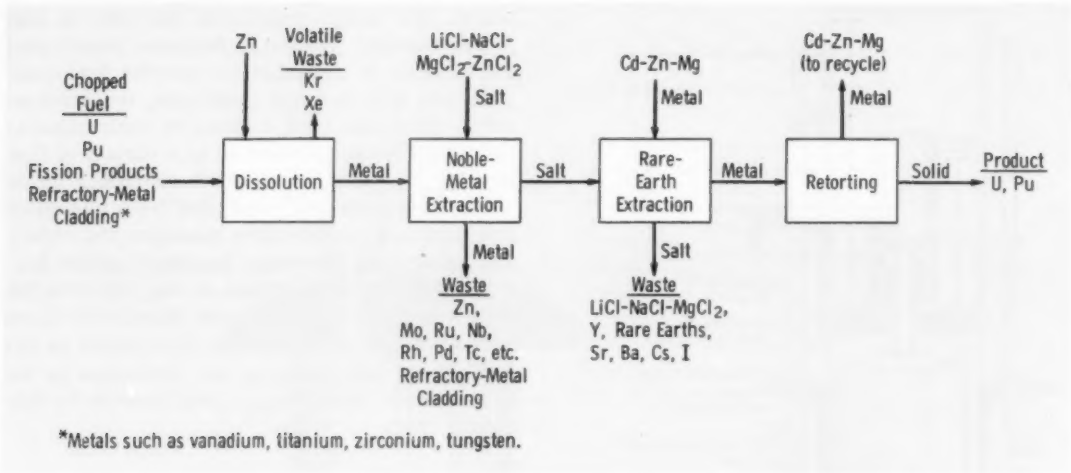


Fig. III-14 Conceptual pyrometallurgical process for uranium-plutonium alloy fuel.[4]

found to be stable in type 304 stainless steel[27] (stability in a 400 series steel is under investigation).

Other published information relating to the rare-earth extraction step includes: (1) the temperature dependence of uranium solubility in the ternary alloy,[4] (2) the effects of temperature and salt- and metal-phase compositions on distribution coefficients,[4] (3) the nature of intermetallic compounds in equilibrium with saturated solutions,[26] (4) corrosion resistance to ternary metal-halide salt systems,[27] and (5) the liquidus temperatures of ternary salt systems.[4,25]

During the course of the above studies, the distribution coefficients of transuranium elements between molten $MgCl_2$ and zinc-magnesium alloys have been determined.[4] The distribution coefficients shown in Fig. III-16 could be employed in an extraction scheme to effect the separation of certain transplutonium elements from each other.

Mullins and coworkers[41] of Los Alamos Scientific Laboratory (LASL) have reported on the development of an electrorefining process for recovery of plutonium from plutonium-iron alloys on a 3.5-kg scale. Such alloys, in particular a 2.5 wt.% iron–plutonium alloy, have been used as molten fuel alloys in the Los Alamos Molten-Plutonium Reactor Experiment (LAMPRE-I). Plutonium metal containing <35 ppm iron and <100 ppm of detectable impurities was produced. With the alloy containing 2.5% iron, the plutonium yield was approximately 82%.

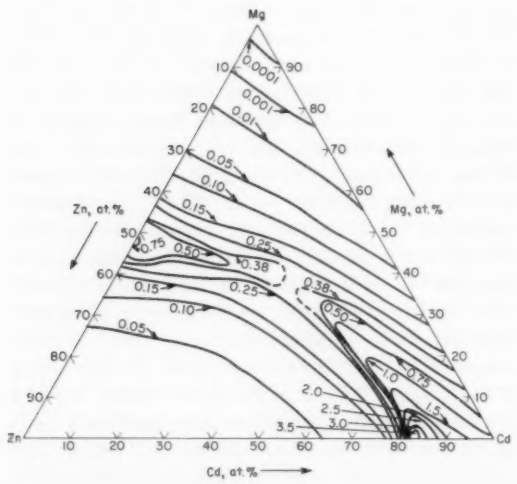


Fig. III-15 Solubility of uranium in cadmium-zinc-magnesium alloy[4] *at 600°C. (Isosolubility lines are given in atomic percent.)*

Miscellaneous Process Information

The behavior of copper in a molten bismuth-LiCl-KCl system has been investigated by Yamagishi and Kamemoto.[42] The distribution of copper between these phases was investigated at 550°C in air and argon atmospheres with and without an oxidant ($BiCl_3$) and a reductant (Mg).

Teitel has been issued a patent[43] on the processing of thorium-bismuth and thorium-lead compounds for recovery of entrapped ^{233}U

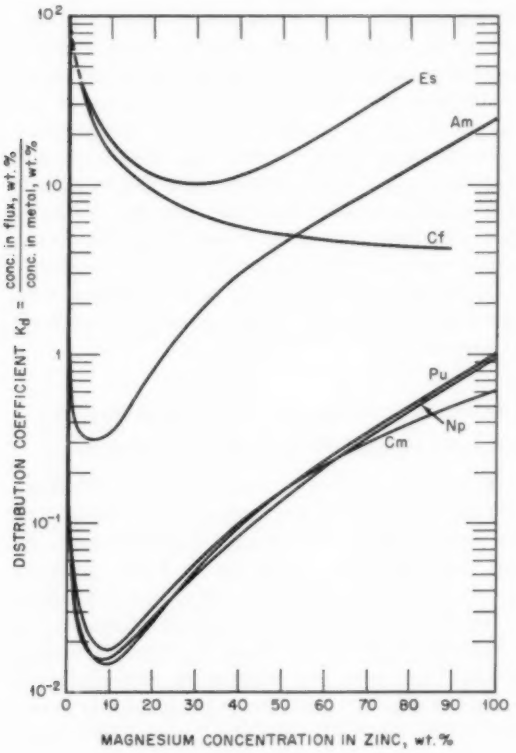


Fig. III-16 Distribution of transuranium elements between magnesium chloride and zinc-magnesium alloy.[4] Conditions: temperature, 800°C; mixing rate, 300 rpm; crucible, tantalum; atmosphere, argon. (Einsteinium measurements were made in alumina crucibles at a temperature of 710°C.)

bred in the thorium. The procedure is directed to the processing of a mobile blanket consisting of a slurry of the above compounds in bismuth. Release of the uranium is effected by changing the temperature to convert the intermetallic compounds into different ones.

A patent has been awarded Chiotti[44] on the regeneration of fission-product-containing thorium-magnesium alloys. The procedure involves selective extractions of impurity and product elements by molten-salt and molten-metal phases.

Preparation of Metals by Reduction of Their Compounds

The processes employed for reduction of reactive metals, such as thorium, uranium, and plutonium, are often closely related to steps employed in pyrometallurgical processes. Lacey and coworkers of the British Atomic Energy Research Establishment at Harwell have examined on a laboratory scale a number of semicontinuous procedures for the reduction of uranium salts to metal.[45] These procedures included electrolysis of uranium-bearing halide salts onto a liquid-metal cathode (and subsequent vaporization and recycle of the solvent metal) and countercurrent contacting of a uranium-bearing salt melt by a solvent containing a reductant such as magnesium.

Kesterke, Fleck, and Henrie of the Bureau of Mines have electrowon uranium metal from uranium dioxide dissolved in fluoride melts composed[46] of LiF, BaF_2, and UF_4. Fed continuously and directly to the cell, the UO_2 was electrolyzed at 1200 to 1300°C to produce a single regulus of uranium metal having a purity as high as 99.8%. Compartmented cells were studied as a means of confining the oxide feed to the vicinity of the anode.

The effect of agitation on the rates of reactions occurring between liquid-metal and salt phases, e.g., reduction of uranium or thorium oxide in liquid-metal–salt systems, is under study at ANL.[4] Agitation has been shown to be an important variable affecting the rates of the reduction reactions. From studies with mercury-water systems, it was found that the greatest dispersion of the phases was obtained with an upward-deflecting impeller located just below the interface.

Conner of the Dow Chemical Co. has published a survey of the literature issued between 1950 and 1963 on the reduction of plutonium compounds.[47] The following patents have been issued on various reduction processes:

1. Reduction of Uranium Oxide in a Zinc Alloy Medium[48] to R. J. Teitel
2. Extraction of Refractory Metals from Their Halides to M. P. Hnilicka, Jr.[49]

Equipment

An eddy-current induction probe under development at ANL[4] shows considerable promise for the remote determination of molten-metal levels. The probe consists of dual-wound, primary and secondary, Nichrome coils on a ceramic core. The output of the secondary coil is strongly affected by the presence of a surrounding conductor. A particular advantage of the eddy-current induction probe is that it operates within a well similar to a thermocouple well. Therefore it can be easily removed for repair or replacement.

Fundamental Studies Relative to Liquid-Metal Process Development

Considerable fundamental information has been accumulated for liquid-metal and salt systems that are used as processing media for nuclear fuels. The logical design of pyrometallurgical processes requires a strong base of fundamental information.

Cadmium is a potential solvent for plutonium and uranium. The solubility of plutonium in cadmium has recently been[4] redetermined (Fig. III-17), and the thermodynamic properties of the plutonium-cadmium system have been determined.[4] Thermodynamic studies of the lanthanum-cadmium and technetium-zinc system have also been reported.[4]

Foster and coworkers at ANL have published evidence[50] for the existence of an intermetallic species (Li_3Bi) in a molten LiCl-LiF salt. This first observation of the existence of an intermetallic species in a molten salt is based on solubility and spectral measurements.

A study of mass transfer of uranium to flowing cadmium has been published by Traylor as a Ph.D. thesis.[51] The rate of mass transfer from $\frac{1}{2}$-in.-diameter uranium spheres (one sphere used in each run) to cadmium flowing around the spheres in a $1\frac{1}{2}$-in. type 304 stainless-steel pipe was investigated as a function of flow rate and prior metallurgical treatment of the uranium. A pronounced "hump" in the curve of mass-transfer factor, J_d (a dimensionless group that includes the mass-transfer coefficient and the physical properties of the cadmium solvent), occurred at Reynolds numbers of about 7×10^4 (see Fig. III-18). Mass-transfer rates were strongly affected by previous metallurgical treatments. Uranium spheres that had been quenched from the beta-phase region (667 to 775°C) to produce fine, randomly oriented grains dissolved more rapidly than spheres with coarse grains having a preferred orientation.

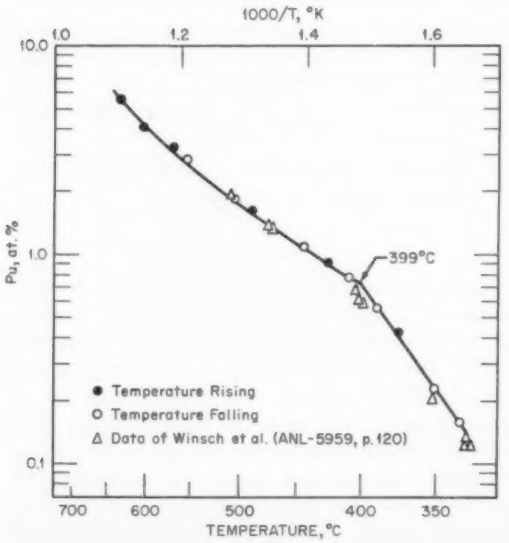


Fig. III-17 Solubility of plutonium in liquid cadmium.[4]

Construction Materials for Liquid-Metal Fuel or Liquid-Metal Process Systems

A major objective of the Los Alamos Molten-Plutonium Reactor Experiments (LAMPRE) is the evaluation of container combinations. At the present time, emphasis is being given to out-of-reactor corrosion tests, but evaluation of corrosion of tantalum capsules used in the LAMPRE reactor is continuing.[52] Intergranular penetration was not evident in any unalloyed tantalum capsules, whereas intergranular penetration in the weld area was present in a number of tantalum–0.1 wt.% tungsten alloy capsules. A number of capsules (one unalloyed tantalum capsule and six alloy capsules) exhibited platelet formation in the weld zone. This is believed to be associated with attack by sodium of oxygen-contaminated tantalum.

Out-of-pile corrosion tests have been concerned with the evaluation of unalloyed tantalum (both electron-beam and double-arc melted) and of tantalum and tantalum–0.1 wt.% tungsten alloy capsules with yttrium additions.[52] The addition of yttrium probably constitutes a deoxidation treatment since very little yttrium remains in the final metal. The alloy capsules containing added yttrium have shown excellent corrosion resistance to a plutonium-iron (2.5 wt.%) alloy. At 650°C three capsules reached 3500 hr and one capsule reached 6300 hr without failure; at 700°C two capsules reached 2800 hr without failure. All untreated alloy capsules failed within 700 hr at either temperature. The yttrium treatment has not been effective for unalloyed tantalum. This difference is not understood and is being further investigated.

Corrosion of tantalum and tantalum alloys by a plutonium-cobalt-cerium alloy containing 5 g

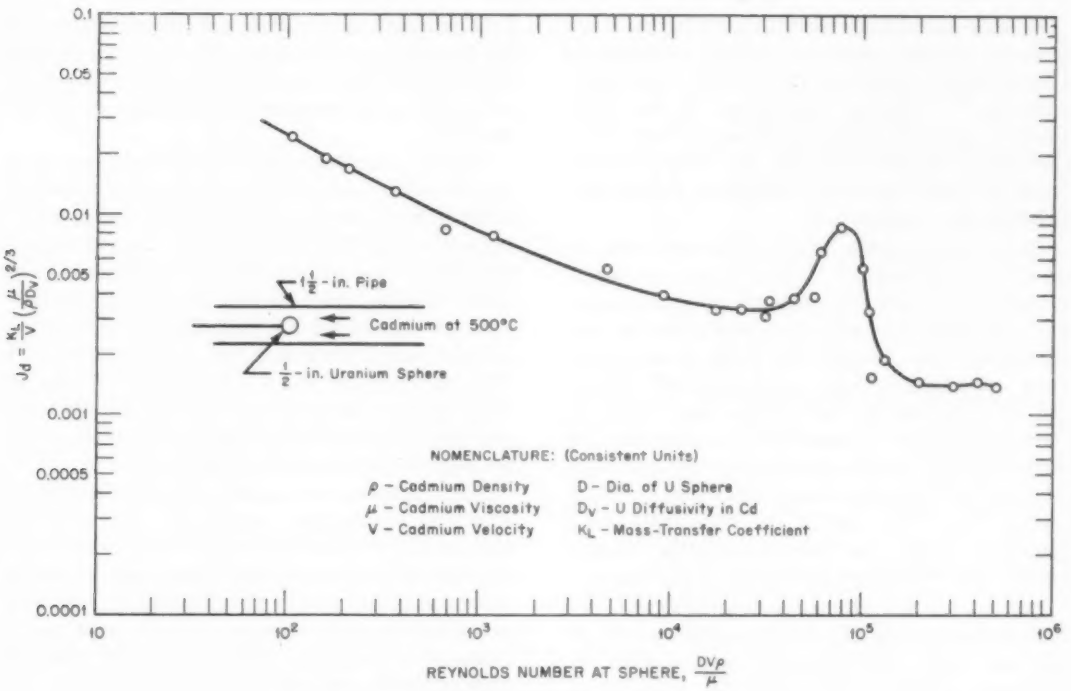


Fig. III-18. Correlation of data for mass transfer from uranium spheres to flowing cadmium.[4]

of plutonium per cubic centimeter is also being investigated.[52] The ternary alloy is much less corrosive than the plutonium-iron alloy.

Weeks of Brookhaven National Laboratory has discussed corrosion mechanisms in liquid metals (alkali metals and bismuth, lead, and mercury).[53] Cleary has discussed the use and performance of refractory metals for containment of alkali metals.[54] (L. Burris, Jr.)

Other Nonaqueous Processes

Pyrochemical processes that employ dry, high-temperature chemical conversions are being developed for the recovery of fissile and fertile material from irradiated oxide and carbide fuels. Gases, molten salts, and liquid metals are generally used as reagents and process media. Since these materials are not subject to significant radiation damage, such processes are particularly suited to closed-cycle low-decontamination processing of short-cooled high-burnup fuels.

Oxide Fuel Processing

At Hanford, research and development studies have continued on the salt-cycle process, which is associated with the Plutonium Recycle Test Reactor (PRTR).[55–58] In the salt-cycle process, the mixed uranium dioxide–plutonium dioxide fuel is declad mechanically and then oxidized in air to convert the uranium dioxide to U_3O_8. The change in volume of the oxide during oxidation results in its pulverization. The powder is dissolved in a molten chloride such as LiCl-KCl by sparging the system with a mixture of hydrogen chloride and chlorine. Either of two methods may be used to recover the dissolved uranium and plutonium oxides from the salt solution. The first entails selective electrodeposition of essentially plutonium-free uranium dioxide, followed by codeposition of uranium dioxide and plutonium dioxide. This procedure causes the codeposited product to be considerably enriched in plutonium. The other method involves selective chemical precipitation of plutonium dioxide by sparging the melt with an oxygen-chlorine mixture. This step is followed by electrodeposition of uranium dioxide.

Further pilot-plant operations with irradiated uranium dioxide–plutonium dioxide mixtures in a high-level radiochemical facility have been reported.[55–57] During dissolution of the oxide mixture in a LiCl-KCl melt sparged with chlorine and hydrogen chloride, the major fission products volatilized were ruthenium, zirconium-niobium, and antimony.

Three electrolyses were performed with the irradiated material.[55,56] The first, in which hydrogen chloride was used as the sparge gas, was designed to separate the uranium and plutonium. The second and third electrolyses were codeposition runs employing 90% oxygen and 10% chlorine as the sparge gas. The first electrolysis gave a plutonium decontamination factor of 8.0. Fission-product decontamination factors, on a uranium basis, were 500 for ^{137}Cs, 1.5 for ^{95}Zr-^{95}Nb, and 67 for ^{106}Ru-^{106}Rh. On a plutonium basis, the decontamination factors for ^{91}Y and ^{144}Ce were 2.5 and 4, respectively.

The second and third electrolyses produced deposits having plutonium concentrations of 0.34 and 0.32 wt.%, corresponding to plutonium enrichment factors of 0.92 and 0.65. Decontamination factors, based on uranium, were 0.32 for ^{95}Zr-^{95}Nb in the second electrolysis and 1330 for ^{137}Cs, 0.60 for ^{95}Zr-^{95}Nb, and 263 for ^{106}Ru in the third electrolysis. Decontamination factors, on a plutonium basis, in the two runs were 2.7 and 2.0 for ^{91}Y and 8.1 and 5.6 for ^{144}Ce.

In the first of two subsequent codeposition electrolyses, a 40-amp current was used for 39 hr in a melt sparged with 2.7 liters of oxygen per minute and 0.3 liter of chlorine per minute.[57] The product was an 8-lb deposit of mixed oxides with a plutonium content of 1.6 wt.%, corresponding to a plutonium enrichment factor of 1.3. In the second electrolysis the product of the first was oxidized and then charged to the melt along with some additional U_3O_8. Electrolysis for 60 hr under the same conditions as the first run resulted in 8.5 lb of product having a plutonium content of 0.6 wt.% and a corresponding plutonium enrichment factor of 1.1. The oxygen-to-uranium ratios of the products from the two runs were 2.07 and 2.1, respectively.

In connection with the work on irradiated materials, an interesting technique for the direct determination of fuel burnup has been reported.[57] The amount of ^{137}Cs in a normal mixture of radionuclides obtained by the dissolution of fuel elements can be determined directly by beta-gamma anticoincidence measurement of the gamma-ray spectrum. It is claimed that the quantity of ^{137}Cs can be determined with good precision in a two-year-old mixture of fission products.

Further chemical investigations have been performed in support of the salt-cycle process. Since earlier work had indicated that metallic impurities in LiCl-KCl melts might cause chloride contamination of electrodeposited uranium dioxide, the effects of several fission-product oxides on the chloride content of the product were examined.[55,56] However, none of the oxides that were investigated (those of molybdenum, zirconium, ruthenium, cerium, and neodymium) had a significant influence on the degree of chloride contamination.

Spectrophotometric observations of LiCl-KCl solutions containing uranyl(VI) and a small amount of U(IV) have indicated a uranium species that had not been observed previously in molten chloride solvents.[55,56] The hypothesis has been proposed that this species is singly oxygenated pentavalent uranium ($UOCl_3$ or $UOCl_5^{2-}$) that is formed by the reaction

$$UO_2Cl_2 + UCl_4 = 2UOCl_3$$

The identity of the species and the proposed reaction are supported by the experimental observation that the concentration of the species is proportional to the square roots of the uranyl(VI) and U(IV) concentrations.

An equilibrium constant for the reaction

$$UO_2 + UO_2Cl_2 = 2UO_2Cl$$

has been derived by a rigorous method from electrochemical data on the reaction.[57] In a NaCl-KCl melt at 713°C, the reported value for the equilibrium constant is $1.2 \pm 0.4 \times 10^{-2}$.

The behavior of plutonyl(V) and plutonyl(VI) species in molten chloride solvents has been reported previously.[59] Some additional details are reported in a recent publication by Swanson.[60] Both plutonyl(V) and plutonyl(VI) species were observed spectrophotometrically in molten LiCl-CsCl solutions of Pu(III) and Pu(IV) that had been sparged with an oxygen-chlorine mixture. When the chlorine was removed from the melt by helium sparging, diminution of the plutonyl(VI) and growth of the plutonyl(V) peaks were evident, and plutonium dioxide finally began to precipitate from the solution. This be-

havior is consistent with the equilibrium reactions

$$PuO_2Cl_2 = PuO_2Cl + \tfrac{1}{2}Cl_2$$

$$PuO_2Cl = PuO_2 + \tfrac{1}{2}Cl_2$$

When the solutions were sparged with oxygen-chlorine mixtures, the plutonyl(V)-to-plutonyl(VI) ratio varied inversely with the chlorine concentration in the sparge gas. With a fixed oxygen-to-chlorine mixture, this ratio increased with temperature and was greater in the LiCl-KCl eutectic than in the LiCl-CsCl eutectic. Sparging with chlorine alone caused reduction of the plutonyl species to Pu(III). A comparison of the spectra of the various plutonium species is given in Fig. III-19.

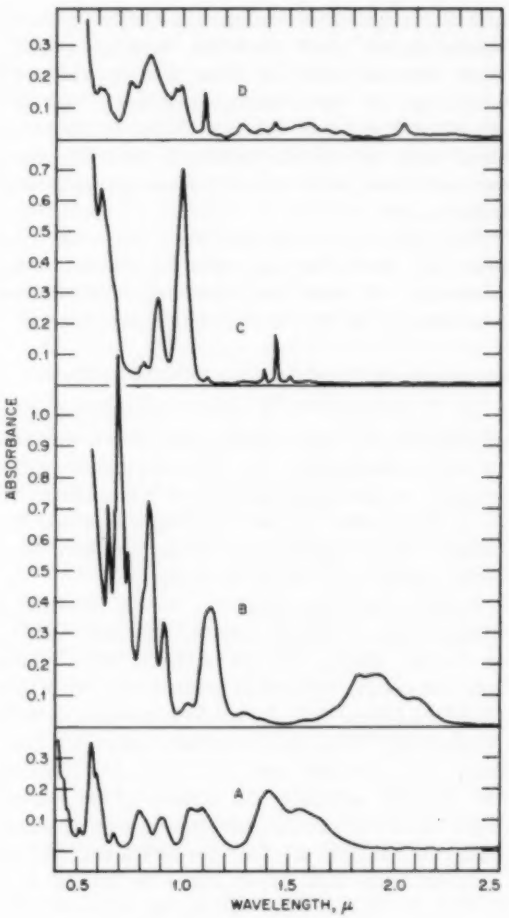


Fig. III-19 Absorption spectra of Pu ions in LiCl-CsCl eutectic[60] at 400°C. A is Pu(III), B is Pu(IV), C is predominantly plutonyl(VI), and D is predominantly plutonyl(V). (Reprinted with permission from the Journal of Physical Chemistry.)

Oxide Precipitation Process at Mol, Belgium

Continuing work at Mol, Belgium, on a process for the conversion of uranium and plutonium fluorides to the oxides in molten chloride solvents has been reported.[14] The objective of the process is to oxidize the fluorides in a salt such as the LiCl-KCl eutectic or the NaCl-KCl-$MgCl_2$ eutectic, thereby precipitating the plutonium from the solution as plutonium dioxide and forming a soluble uranium oxyhalide. The uranium can then be recovered either by chemical precipitation of uranium dioxide or by electrolytic reduction.

The chemical precipitation technique was investigated in a series of experiments in which 26 g of uranium tetrafluoride was added to 110 g of molten LiCl-KCl eutectic, the melt was dried by chlorine sparging for 20 min, and then the system was sparged with oxygen for 4 hr. Reduction of the mixture with hydrogen for 8 hr produced uranium dioxide with oxygen-to-uranium ratios of 2.06 to 2.16 in yields varying from 57 to 71%. The bulk of the products had a particle size greater than 75 μ.

The use of a metal as a reductant has been suggested in order to avoid harmful effects of water produced as a by-product of the hydrogen reduction, i.e.,

$$UO_2Cl_2 + M = UO_2 + MCl_2$$

When tin with a density of 6.5 g/cm^3 and a melting point of 232°C is used as the reductant, the precipitated uranium dioxide with a density of about 10.9 g/cm^3 becomes separated from the supernatant salt by an intermediate layer of liquid tin.

Electrodepositions of uranium dioxide from uranyl chloride solutions were also performed, using the LiCl-KCl and NaCl-KCl-$MgCl_2$ eutectics as solvents. The uranyl chloride solutions were prepared by adding about 25 g of uranium dioxide to 300 g of the salt and then sparging the mixture with hydrogen chloride and oxygen at temperatures of 495 to 550°C. The electrodepositions were performed with hydrogen chloride sparging at temperatures of 495 to 500°C and at potentials of 1.5 to 2.0 volts. Uranium dioxide recoveries as high as 79% were achieved,

and the oxygen-to-uranium ratios of the products varied from 2.003 to 2.014. Similar results were obtained when uranium tetrafluoride was employed as the starting material, and the uranyl species was formed either by sparging first with an oxygen–hydrogen chloride mixture and then with oxygen or by sparging only with oxygen.

The authors indicate that the results obtained thus far leave the way open for further consideration of both the chemical precipitation process and the electrodeposition process.

Uranium and Protactinium Oxide Precipitation Process

At Oak Ridge[61] a conceptual two-region molten-salt breeder reactor has been described in which fissionable ^{233}U is recovered from the blanket as the decay product of ^{233}Pa. Removal of protactinium, as well as uranium, from the blanket is desirable to decrease parasitic neutron capture by ^{233}Pa in the blanket.

Small-scale experiments were conducted using a molten fluoride mixture (67 mole % LiF, 18 mole % BeF_2, and 15 mole % ThF_4) which was considered typical of blanket materials that may find future use. Irradiated thorium dioxide (containing ^{233}Pa) and, in some instances, uranium tetrafluoride and/or ^{231}Pa were added to the fluoride mixture. All oxides in the system were converted to fluorides by hydrogen fluoride sparging at 650°C. The protactinium and/or uranium was then precipitated by adding 1 to 2 wt.% of calcium, beryllium, thorium, or uranium oxide to a 500-g batch of the melt at 650°C. Equilibrium was apparently reached within 2 hr. A single batch of the melt could be reused for several experiments by reconverting the precipitated oxides to fluorides through hydrogen fluoride sparging.

Protactinium was effectively removed from the melt by additions of beryllium oxide or thorium oxide when the initial protactinium concentration was either in the range of 1 to 2 ppb or 50 to 75 ppm. Uranium was also removed from the solution by oxide additions, but somewhat less readily than protactinium. The presence of uranium appeared to enhance the removal of protactinium by beryllium oxide.

The ease with which the precipitated oxides could be redissolved by hydrogen fluoride sparging suggests a simple blanket process in which the uranium and protactinium would be precipitated and recovered, and then the blanket mixture would be treated with hydrogen fluoride and returned to the reactor. No detectable amounts of protactinium were volatilized when the melts were sparged with helium, hydrogen, or hydrogen fluoride.

Gaseous Low-Decontamination Process for Uranium Dioxide Fuels

The AIROX process, under development at Atomics International, is a closed-cycle low-decontamination process for uranium dioxide fuels which uses simple gas-solid reactions.[62–64] The fuel is declad and pulverized by alternate oxidation with air or dilute oxygen at 200 to 600°C and reduction with hydrogen at 600°C. The powdered product is reenriched by blending and refabricated by cold pressing and sintering. Fission-product removal is insignificant, the objectives of the process being limited to the repair of irradiation damage and reenrichment of the fuel.

Fuel pellets made from irradiated uranium dioxide (5700 to 21,000 Mwd/metric ton) which had previously been processed and refabricated have been reirradiated in the MTR for an additional 10,000 Mwd/metric ton. Other fuel pellets containing additions of stable oxides of fission-product elements (fissia) to simulate a burnup of 100,000 Mwd/metric ton were also irradiated to 5000 Mwd/metric ton. Postirradiation examinations of both types of fuel have been reported.[62–64] It was concluded that the processed, reirradiated uranium dioxide and the uranium dioxide–fissia mixture show the same behavior under irradiation as production-grade uranium dioxide. Some reduction in thermal conductivity resulting from the presence of fission products might have occurred.

Pertinent to the oxidation step of the AIROX process is some recently reported work in Germany on intermediate phases that are formed[65] during the oxidation of uranium dioxide to U_3O_8. At temperatures of 160 to 220°C, the initial oxidation produced shells of U_3O_7 around the uranium dioxide particles. Further oxidation at 280 to 290°C occurred by diffusion of oxygen through these shells to form U_5O_{12}. At 375 to 400°C the oxidation continued, forming U_5O_{13}, and, finally, U_3O_8.

Carbide Fuel Processing

The development of simple low-decontamination processes for the recovery of uranium carbide fuels has continued at Atomics Inter-

national.[62–64,66] The main emphasis is currently being applied to an oxidation-carbothermic reduction cycle (CARBOX process). This process comprises a low-temperature oxidation of the uranium carbide fuel by oxygen, air, or steam, followed by reaction of the oxide product with carbon at about 1500°C to regenerate the uranium monocarbide. Although arc melting has been employed as the primary method of fuel refabrication, other techniques are receiving attention because of volatile plutonium losses at arc-melting temperatures.

Further scale-up studies have been conducted on the oxidation of uranium monocarbide in batches up to 10 kg. Earlier work had shown that air oxidation of the carbide proceeds much more readily if it is first "activated" by exposure to water vapor in the form of moist air. However, some difficulty has been encountered in achieving sufficient activation of large (up to 5 kg) batches of hypostoichiometric (carbon-deficient) uranium monocarbide.[62,66] When material that was previously difficult to activate was arc melted, the product was activated readily. Since small samples of the carbide were found to be highly stressed after arc melting, it is suspected that a phenomenon similar to stress corrosion may be involved in the activation process.

A rotary-kiln furnace has operated satisfactorily in the air oxidation of 10-kg batches of uranium monocarbide. In oxidations of 3- to 11-kg batches of cast, hypostoichiometric (4.6 wt.% carbon; theoretical for UC, 4.80 wt.%) uranium monocarbide, the −200-mesh fraction, amounting to 50 to 90% of the product, was a uniform material suitable for reconversion to the carbide. On a cumulative basis, no buildup of material in the furnace occurred, once a heel estimated to be about 200 g was established. A continuing effort is under way to resolve the problem of satisfactorily activating hypostoichiometric uranium monocarbide. Some progress has been made in the form of a rapid procedure by which 70 to 80% of a batch of carbide can be activated in a 24-hr period. Also under investigation are methods for decreasing further the residual carbon content of the oxide product and the possibility of controlling the oxidation reaction by monitoring the carbon dioxide content of the off-gas.

Scale-up studies are also continuing on the carbothermic reduction step of the CARBOX process.[63,64] Uranium carbide of controlled composition by the carbothermic reduction of U_3O_8 has been demonstrated. The use of U_3O_8 instead of UO_2 as a starting material appears to have no disadvantages. Some loss of uranium by vaporization was noted when hypostoichiometric uranium monocarbide was prepared by heating U_3O_8-carbon mixtures to a final temperature of 1900°C. It appears that complete removal of oxygen from the product is more difficult in the preparation of hypostoichiometric carbide than for a stoichiometric or carbon-rich product. The experimental results indicated that an oxygen content of less than 500 ppm was difficult to achieve in the preparation of hypostoichiometric uranium monocarbide.

Small-scale investigations have continued on the effect of sintering aids on the density of uranium monocarbide prepared by carbothermic reduction of U_3O_8 and uranium dioxide.[62–64,66] Without the sintering aids, uranium dioxide–carbon mixtures yielded a product with a density (after crushing) of 95% of theoretical, whereas U_3O_8-carbon mixtures resulted in a product density of about 90% of theoretical. The effects of various sintering aids, including UAl_2, UFe_2, and UNi_2, which were reported previously,[67] and tungsten, molybdenum, and palladium have been studied. These latter metals, which probably remain in the product, increased the density of uranium monocarbide prepared either from U_3O_8 or uranium dioxide. In the case of UFe_2, the iron is almost completely vaporized during the reaction, whereas nickel added in the form of UNi_2 was partially retained. When UFe_2 and UNi_2, which are liquid at the reaction temperature of about 1500°C, were used, the grain size of the product was increased as much as a factor of 5. These additives have the advantage that a slight excess of carbon can be used to reduce the residual oxygen content, while the additional uranium still results in a hypostoichiometric product. The two eutectic alloys, uranium–11 wt.% iron (melting point 725°C) and uranium–11 wt.% nickel (melting point 740°C), had approximately the same effect as the intermetallic compounds, yielding products having 94 to 97% of theoretical density after crushing.

The effect of final temperature on the density and composition of the product resulting from U_3O_8-carbon pellets containing UAl_2 and UNi_2 is shown in Table III-2. The higher temperatures gave only a slight improvement in the density, but no improvement in the oxygen con-

Table III-2 EFFECT OF TEMPERATURE ON DENSITY AND OXYGEN CONTENT OF URANIUM MONOCARBIDE PRODUCED[64] BY CARBOTHERMIC REDUCTION OF U_3O_8

Additive*	Final temp., °C	Carbon,† wt.%	Oxygen, wt.%	Product density, g/cm³
UAl_2	1650	4.55 ?	0.15	13.15
UAl_2	1750	4.55	0.12	13.20
UNi_2	1550	4.50	0.09	13.00
UNi_2	1650	4.50	0.10	13.14
UNi_2	1750	4.50	0.10	13.21

*The quantity of additive corresponded to 8 at.%.
†Theoretical for UC, 4.80 wt.%.

tent, indicating that it is advantageous to use the lower temperatures where volatilization losses of uranium and plutonium are minimized. Of the reductions completed to date, the highest density reported is 13.32 g/cm³, or 97% of theoretical, which was obtained with 4 at.% iron as UFe_2.

Plutonium volatilization during the carbothermic reduction step is undesirable, since plutonium retained in the fuel helps to offset losses of reactivity resulting from fission-product poisons and ^{235}U consumption. Use of a helium atmosphere instead of vacuum appeared to have no effect on cerium losses by vaporization in an experiment using cerium as a stand-in for plutonium. However, the slight excess of carbon that can be used with sintering aids such as UFe_2 may decrease the degree of plutonium volatilization.

Although use of a helium atmosphere did not appear to affect the vaporization of plutonium, it did influence the kinetics of the reduction. The reaction rate tended to decrease near the end of the reaction, indicating a behavior more like that of a first-order reaction than the second-order rate behavior observed under vacuum. In one case the reaction under a helium atmosphere was essentially complete after a total heating time of 4 hr and a maximum temperature of 1900°C. (R. K. Steunenberg)

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Section

IV

Reactor Fuel Processing

Waste Disposal

Liquid-Waste Treatment by Ion Exchange and Foam Separation

Ion Exchange

Highly radioactive aqueous wastes are produced in fuel-processing operations at the Savannah River Laboratory. These wastes are evaporated, neutralized with sodium hydroxide, and stored at about 35 wt.% total solids in large underground tanks that are equipped with cooling facilities to remove heat generated by radioactive decay. The alkaline waste separates into two fractions during storage: (1) a sludge layer that contains most of the biologically hazardous radioactive elements, such as ^{90}Sr and ^{239}Pu, and (2) a supernatant layer that contains, after about six years, ^{137}Cs as the principal (>99%) radioactive element. Additional reduction in volume and more economical storage are achieved by concentration of the supernatant layer of aged stored alkaline wastes in an evaporator to about 75 wt.% total solids, and the concentrated supernatant is then stored in large uncooled tanks. The evaporation step produces a dilute alkaline condensate that contains radioactive ^{137}Cs and other inactive constituents. The composition of this condensate is shown in Table IV-1. After the condensate is monitored, it is discharged to seepage basins; ^{137}Cs in the condensate constitutes a large fraction of the total gamma activity discharged. Prout and Russell[1] at Savannah River have reported on a single-cycle ion-exchange process for removing ^{137}Cs from this condensate prior to its disposal to the seepage basin. Laboratory tests were first conducted to determine which ion-exchange material would be most suitable for this process. On the basis of laboratory tests, two of the most promising absorbents, Decalso* and Duolite C-3,† were selected for plant tests. The plant tests were carried out at a feed flow rate of 4 ml/(min)(cm^2). Although both absorbents gave excellent removal (~99%) of cesium, the volumetric capacity for the condensate was greater for the Decalso (9000 bed volumes) than for the Duolite C-3 (5000 bed volumes). In the proposed flow sheet (see Fig. IV-1) for the plant installation, a 21-in.-diameter column containing 60 gal of Decalso is provided. It is capable of processing 600,000 gal of condensate at a flow rate of 10 gal/min. The condensate is filtered before passage through the column. The effluent from the column, containing an average of only 1% of the cesium in the condensate, is then transferred to seepage basins. The cesium-loaded Decalso may be either discharged directly to the uncooled waste tank (see Fig. IV-1) for receiving evaporator concentrate or regenerated by eluting the absorbed cesium with about 5 bed volumes of $4M$ NH_4NO_3 at 25°C or with about 10 bed volumes of $4M$ $NaNO_3$ at 70°C. The eluted cesium is sent to the concentrate waste tank. Some Decalso must be added after each operating cycle because Decalso is slightly soluble in the alkaline condensate.

At Brookhaven National Laboratory, work is being carried out on the application of ion-exchange processes for the decontamination of cesium from high-level-activity alkaline supernatant waste solutions at Savannah River. Katz and Rothbart[2] describe the development of a flow sheet that utilizes Linde AW-400 molecular

*An inorganic absorbent of the aluminosilicate type; a product of the Ionac Chemical Corporation of the Permutit Co.

†An organic absorbent of the sulfonated phenolic type; a product of the Chemical Process Co.

Table IV-1 COMPOSITION OF EVAPORATOR CONDENSATE[1]

[pH = 10.5; Gamma Activity* = 1×10^4 to 2×10^4 dis/(min)(ml)]

Constituent	Concentration, mg/liter
NH_4OH	200
$NaNO_3$	85
$NaAlO_2$	15
KNO_3	2.6

*Ninety-five percent of the gamma activity is from ^{137}Cs; the balance is mostly from ^{106}Ru.

sieves. The process provides effective decontamination of cesium (and probably strontium) from supernatant waste solutions containing potassium and aluminum. The proposed flow sheet is shown in Fig. IV-2. Of the various ion-exchange materials investigated, Linde AW-400 was the only one that had sufficient cesium capacity in the presence of 0.05*M* potassium to be of practical consideration. Ions other than potassium and sodium in the waste solution do not affect the cesium capacity. Sodium aluminate (0.04*M*, minimum concentration) must be added to the waste to prevent chemical attack of Linde AW-400 by the highly alkaline waste. In addition, an ammonia rinse of the column is necessary prior to the introduction of fresh waste solution to prevent precipitation of sodium aluminate on the ion exchanger after the elution portion of the cycle. With the use of actual plant-level-activity alkaline supernatant solution from Savannah River and Linde AW-400, excellent removals (>99%) for cesium were obtained. Strontium was not detected in the feed material.

Harwell Investigation of Centrifuged-Bed Technique for Decontamination of Radioactive Effluent

At Harwell, experimental work has been carried out on the use of the centrifuge as a means for obtaining high flow rates through a bed of vermiculite without greatly affecting its ion-exchange properties. This centrifuged-bed technique was originally developed at Mol (Belgium) where it had been used to overcome the poor flow characteristics of lignite used in the treatment of radioactive effluents. Clarke and associates[3] at Harwell have published the results of laboratory and pilot-plant experiments in which centrifuged beds of vermiculite (crude grade; initially converted to sodium form) were used to remove ^{137}Cs from a solution that simulated Harwell plant effluent after chemical treatment with trisodium phosphate and ferrous sulfate at *p*H 11.5 (solutions consisting of demineralized water containing 300 mg of sodium per liter and added ^{137}Cs tracer at *p*H 11.5) and from actual Harwell plant supernatant waste of medium-level activity which had also received chemical treatment with Na_3PO_4 and $FeSO_4$. Problems of channeling in the vermiculite bed and of uneven distribution of the feed solution

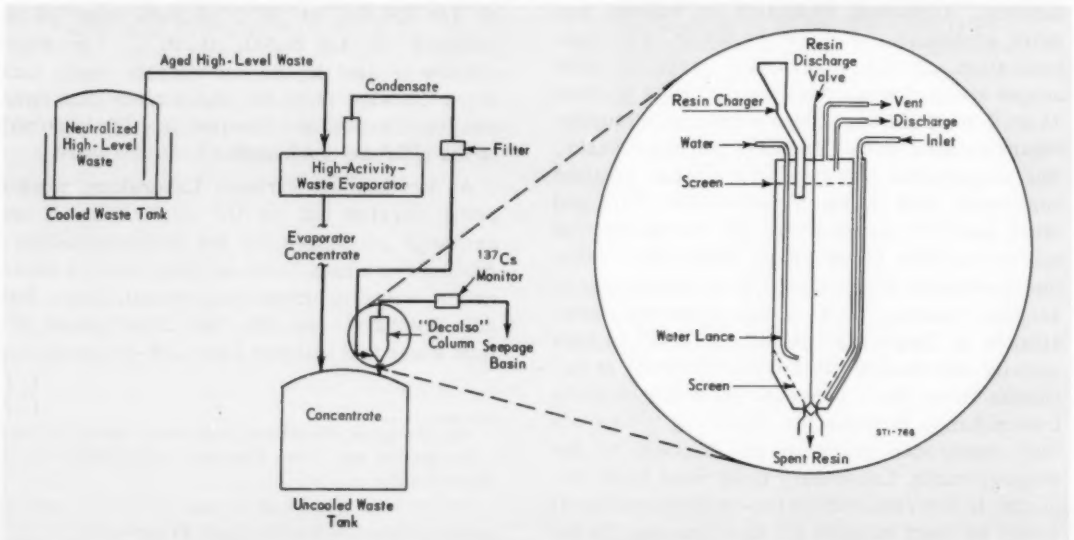

Fig. IV-1 Flow sheet for removal of cesium from evaporator condensate.[1]

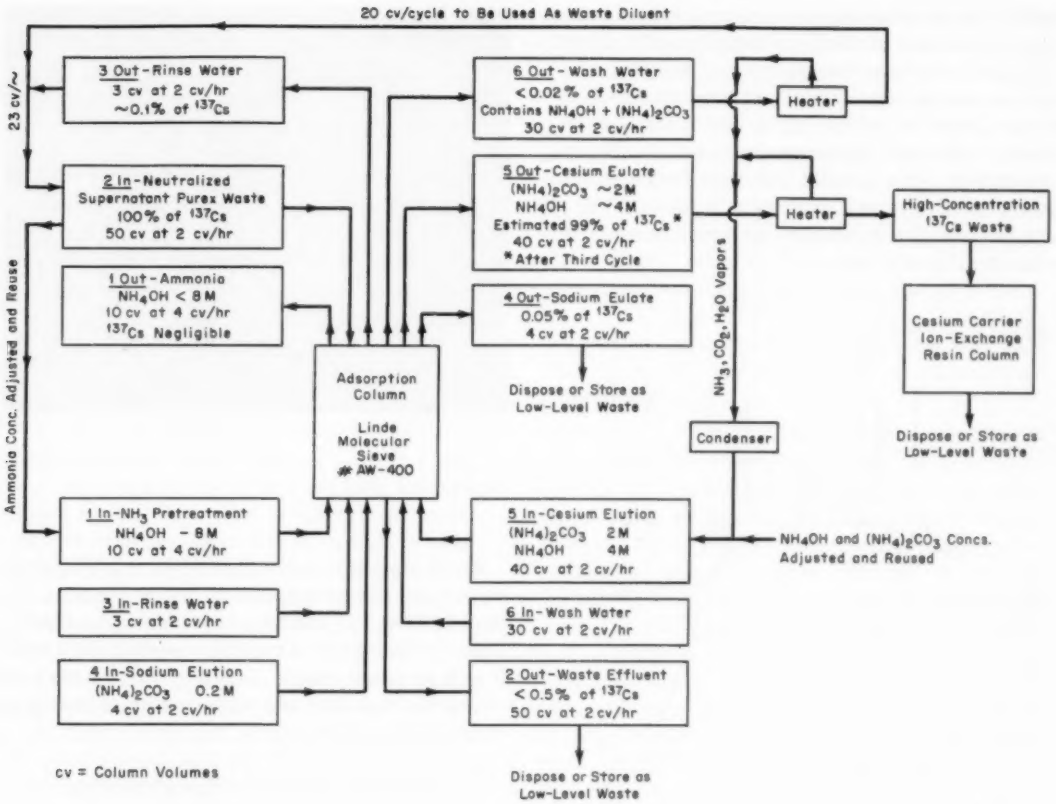
20 cv/cycle to Be Used As Waste Diluent
23 cv/~
3 Out - Rinse Water
3 cv at 2 cv/hr
~0.1% of 137Cs
2 In - Neutralized Supernatant Purex Waste
100% of 137Cs
50 cv at 2 cv/hr
1 Out - Ammonia
NH4OH < 8 M
10 cv at 4 cv/hr
137Cs Negligible
Ammonia Conc. Adjusted and Reuse
1 In - NH3 Pretreatment
NH4OH - 8 M
10 cv at 4 cv/hr
3 In - Rinse Water
3 cv at 2 cv/hr
4 In - Sodium Elution
(NH4)2CO3 0.2 M
4 cv at 2 cv/hr
cv = Column Volumes
Adsorption Column
Linde Molecular Sieve
AW-400
6 Out - Wash Water
< 0.02% of 137Cs
Contains NH4OH + (NH4)2CO3
30 cv at 2 cv/hr
5 Out - Cesium Eulate
(NH4)2CO3 ~2M
NH4OH ~4M
Estimated 99% of 137Cs *
40 cv at 2 cv/hr
* After Third Cycle
4 Out - Sodium Eulate
0.05% of 137Cs
4 cv at 2 cv/hr
Dispose or Store as Low-Level Waste
5 In - Cesium Elution
(NH4)2CO3 2M
NH4OH 4M
40 cv at 2 cv/hr
6 In - Wash Water
30 cv at 2 cv/hr
2 Out - Waste Effluent
< 0.5% of 137Cs
50 cv at 2 cv/hr
Dispose or Store as Low-Level Waste
Heater
Heater
High-Concentration 137Cs Waste
NH3, CO2, H2O Vapors
Condenser
Cesium Carrier Ion-Exchange Resin Column
Dispose or Store as Low-Level Waste
NH4OH and (NH4)2CO3 Concs. Adjusted and Reused

Fig. IV-2 Proposed flow sheet for decontamination of Purex-waste supernatant.[2]

over the bed were satisfactorily solved. The channeling was overcome by two methods: (1) applying in the centrifuge a sufficiently thick precoat of freshly precipitated $BaSO_4$ which would impede the flow of liquid and maintain a wall of liquid over the vermiculite bed; or (2) using a fine grade (97 wt.% <30 mesh) of vermiculite. Even distribution of feed solution was achieved by spraying the feed over the bed by means of a pipe that was perforated along its length and sealed at one end.

The laboratory tests with simulated Harwell effluent were conducted with a vertical bed type centrifuge (see Fig. IV-3). In runs using beds (1.1 cm in thickness) of fine vermiculite and throughput rates of 40 bed volumes/hr (contact time of 90 sec), the ^{137}Cs breakthrough amounted to 0.5% at 400 bed volumes and 2.5% at 2800 bed volumes. The pilot-plant tests were performed with a 10-liter capacity horizontal-bed type basket centrifuge (see Figs. IV-4 and IV-5). The centrifuge was fitted with a scraping knife and chute through which the contents of the basket were discharged. Preliminary tests in the centrifuge established that, prior to depositing the vermiculite in the centrifuge, it was necessary to backwash the vermiculite to remove a claylike material that was believed responsible for reducing the flow of feed through the centrifuge. The pilot-plant decontamination tests were conducted with 5-liter beds (2.4 cm in thickness) of fine vermiculite (crude grade, in the sodium form) and at flow rates of 36 bed volumes/hr (contact time of 100 sec). In a test with synthetic Harwell plant effluent, the ^{137}Cs breakthrough was initially 1.5% and rose to 2.5% at 1600 bed volumes. In a test with actual plant supernatant, the breakthrough of activity was initially 7% and rose to 15% at 1600 bed volumes. Although the activity breakthrough was high in the centrifuged-bed run, the overall removal of activity obtained by chemical treatment com-

bined with the centrifuged-vermiculite-bed technique amounted to 99.7% initially and 99.4% at 1600 bed volumes. These overall activity removals compare very well with those obtained in the plant in which chemical treatment is coupled with ion-exchange columns containing vermiculite. The results obtained in the pilot-plant centrifuged-bed run were considered acceptable. Further scaling up to plant size is considered practicable.

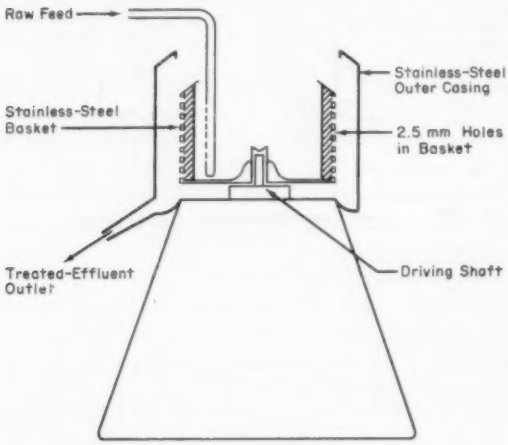

Fig. IV-3 Laboratory-model centrifuge.[3]

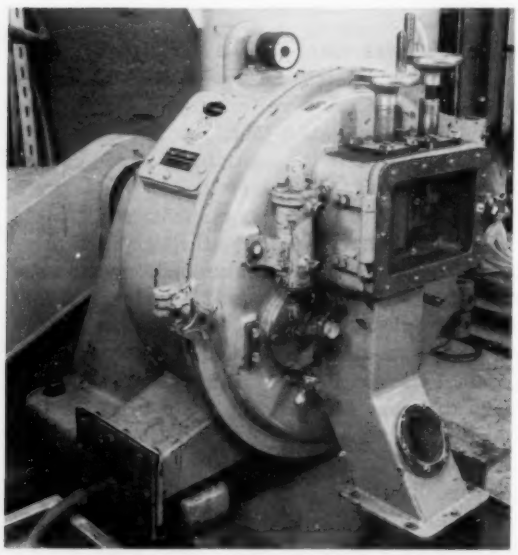

Fig. IV-4 General view of pilot-plant centrifuge.[3]

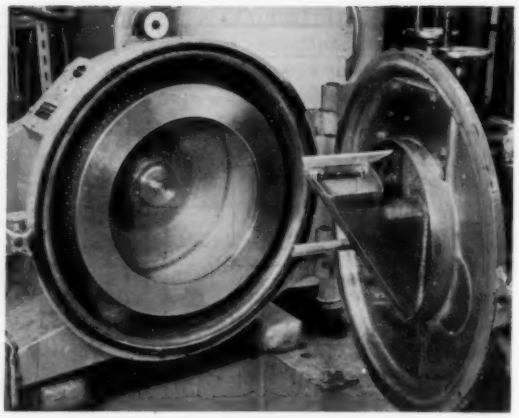

Fig. IV-5 View of open pilot-plant centrifuge showing vermiculite bed.[3]

Future plans include the testing of a 500 gal/hr centrifuge for incorporation into a new plant for the treatment of medium-level-activity effluent. This centrifuge will be of the vertical bed type. It will be fitted with a plough to remove the bulk of the vermiculite and with rinsing facilities to remove the remainder.

ORNL Scavenging-Precipitation Ion-Exchange Process Studies

A scavenging-precipitation ion-exchange process[4] is under development at Oak Ridge National Laboratory (ORNL). The process is intended for the decontamination of the large volumes of slightly contaminated water that originate from many sources in the processing of nuclear fuels. The decontamination is achieved in two steps: (1) a head-end treatment that involves precipitation of a portion of the activity with sodium hydroxide and copperas (ferrous sulfate), clarification of the water in a gently agitated sludge-column clarifier, and filtration of the effluent from the clarifier effluent; and (2) an ion-exchange step (or, alternatively, a foam-separation step, which is discussed in the following subsection) in which the clarified and filtered effluent is passed through a carboxylic-phenolic cation-exchange resin for sorption of about 99% of the ^{137}Cs and ^{90}Sr that has not been removed in the scavenging-precipitation step. The cation resin (after passage of 1500 to 2000 bed volumes of waste) is eluted with 10 bed volumes of 0.5*M* HNO_3, rinsed with water, and regenerated with 20 bed volumes of 0.1*M* NaOH.

In the flow sheet under consideration,[5,6] the acid eluate containing the desorbed activity from the resin-bed elutriation step is to be concentrated in an evaporator. However, the need for an evaporation step could be eliminated (with consequent economies in capital and operating costs), if the major fractions of cesium, strontium, and other activities in the eluate were retained in the sludge blanket of the head-end treatment step.[7] As a means of eliminating this evaporation step, a method of treatment of the acid eluate was investigated which involves adjusting the *p*H of the eluate, admixing grundite clay (which strongly sorbs cesium), and then recycling the resulting slurry with fresh process feed to the scavenging-precipitation portion of the process.

In a laboratory test of this method, 1900 bed volumes of ORNL low-level-activity waste (LAW) were decontaminated by the scavenging-precipitation ion-exchange process described above. The nitric acid eluate from the ion-exchange step was first adjusted to *p*H 3 by the addition of sodium hydroxide and then mixed with grundite clay, after which the resulting slurry was metered into the fresh feed stream (LAW). This combined stream (*p*H adjusted to 11.8) then served as feed to the head-end step of the scavenging-precipitation ion-exchange process. In the subsequent ion-exchange step, 1900 bed volumes of the filtered effluent from the sludge-column clarifier were passed through the resin column. The effluent from the column was found to contain 1.3% of the cesium and <0.3% of the strontium.

The sorption of cesium on grundite clay was also determined in batch tests that investigated the effects of *p*H, grundite particle size, and sequence of grundite addition (before or after *p*H adjustment).[7] The test results showed the following effects on the sorption of cesium on grundite: (1) the optimal *p*H range was quite narrow, about 11.8; (2) the particle size (from about 50 mesh to <200 mesh) of the grundite clay had little effect on the cesium sorption, and (3) the addition of grundite clay prior to *p*H adjustment favored higher cesium sorption.

Foam Separation

ORNL is continuing its investigation of a scavenging-precipitation foam-separation process[7,8] for removing ^{90}Sr from ORNL LAW. (Development work[9] is also being carried out at Radiation Applications Inc., under a contract with ORNL.) The process consists in two steps. The first is a head-end step in which precipitation of hardness ions (calcium and magnesium) is achieved by the addition of 0.005*M* each of hydroxide and sodium carbonate, and coagulation is accomplished with 2 to 5 ppm ferric ion (as ferric chloride), which also serves to reduce the interference effect of phosphates. Subsequent clarification in an upflow sludge-bed filter removes calcium carbonate, magnesium hydroxide, and algae. The second step is a foam-separation procedure for removing the ^{90}Sr. This step is carried out in a countercurrent foam contactor.

At ORNL[7] further investigation has been made of various factors for improving the completeness of phosphate precipitation from LAW. Previous studies[10] showed that the precipitation of calcium (as calcium carbonate) is inhibited by phosphate ion. The large amounts of calcium (60 to 70 ppm as $CaCO_3$) present in the LAW interfere with ^{90}Sr removal by foam separation. In laboratory-scale apparatus the effects of time, *p*H, and method of adding sodium hydroxide and sodium carbonate on the precipitation of phosphate were investigated.[7] Several beaker tests were conducted with LAW containing 4.6 ppm phosphorus (as PO_4^{3-}). In one set of tests in which the effect of *p*H on residual phosphorus was studied, 10 ppm Fe^{3+} (as $FeCl_3$) was added to the LAW and a mixing time of 4 min was used. At *p*H 7, the total soluble phosphorus was reduced to a minimum (0.04 ppm); at *p*H 11.3 (the *p*H value used in the sludge-bed precipitation of calcium carbonate), the total soluble phosphorus was 0.2 to 0.3 ppm. In other beaker tests the effect on residual phosphorus of *p*H (7.2 and 11.4), mixing time, and method of addition of coagulant (Fe^{3+}, 10 ppm) and hardness precipitants (NaOH and Na_2CO_3, 0.005*M* each) was studied. In one of these tests, Fe^{3+}, NaOH, and Na_2CO_3 were added at the same time to the LAW. The final *p*H of the solution was 11.4. In another test, Fe^{3+} was added first, and the solution was mixed for 4 min (during which the *p*H was 7.2), after which the NaOH and Na_2CO_3 were added (final *p*H of 11.4). The results (see Fig. IV-6) of both tests show that the maximum precipitation of phosphate is attained within 1 to 4 min. The results also show that on increasing the *p*H of the waste solution to 11.4 by addition of NaOH and Na_2CO_3 to the solution after the phosphate has been precipitated as ferric phos-

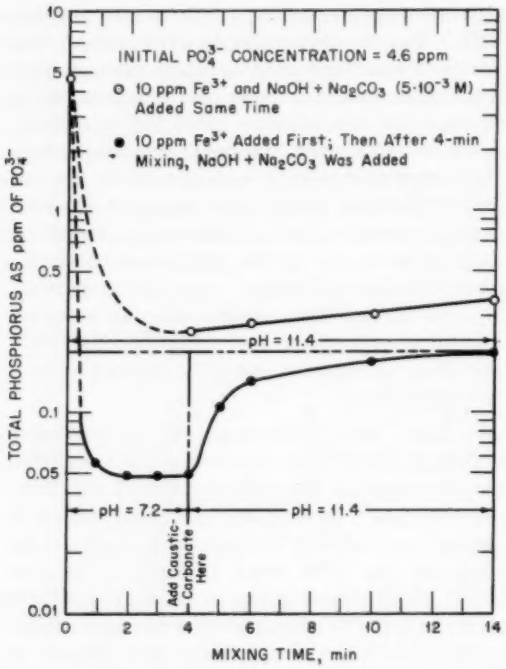
INITIAL PO_4^{3-} CONCENTRATION = 4.6 ppm
o 10 ppm Fe^{3+} and NaOH + Na_2CO_3 ($5 \cdot 10^{-3}$ M) Added Same Time
• 10 ppm Fe^{3+} Added First; Then After 4-min Mixing, NaOH + Na_2CO_3 Was Added
pH = 11.4
pH = 7.2
pH = 11.4
Add Caustic-Carbonate Here
TOTAL PHOSPHORUS AS ppm OF PO_4^{3-}
MIXING TIME, min

Fig. IV-6 Effect of pH and mixing time on the phosphate removal.[7]

phate at *p*H 7.2, the concentration of soluble phosphate in the solution increases. This results from the redissolution of the ferric phosphate with the eventual reprecipitation of the ferric ion as a hydrous oxide. The rate at which the ferric phosphate is redissolved controls the rate at which ferric oxide can precipitate and, hence, the rate at which phosphate ion is liberated. The temporary removal of phosphate ion as ferric phosphate allows the precipitation of calcium carbonate to be more nearly complete. It can also be concluded from Fig. IV-6 that, when Fe^{3+} is added to the essentially neutral LAW, the subsequent deleterious effects of 4 to 5 ppm phosphate on calcium carbonate precipitation at *p*H 11.4 are less than would be observed if the Fe^{3+}, the sodium hydroxide, and the sodium carbonate were added at the same time. The separate addition of precipitation-inducing compounds would make it possible to compensate for unusually large amounts (up to 10 to 15 ppm) of phosphate that occasionally appear (for brief intervals) in LAW at ORNL. The usual concentration of soluble phosphorus in LAW is in the range of 1 to 3 ppm.

Runs[7] were also conducted in a laboratory sludge-bed column at a throughput rate of 20 gal/(hr)(sq ft), with a separate mixing tank (holdup time of 4 min) for premixing of precipitation-inducing reagents (Fe^{3+}, NaOH, and Na_2CO_3) with the waste solution. In these runs, which were carried out with ORNL tap water to which 5 ppm phosphorus was added as sodium orthophosphate, a study was made of the effect of the separate or simultaneous addition of the precipitation-inducing reagents on the residual total hardness (as Ca^{2+}) remaining in the effluent stream from the sludge-bed column. The separate addition of the reagents involved (1) adding the Fe^{3+} to the waste solution being fed to the mixing tank and (2) introducing sufficient NaOH-Na_2CO_3 solution (each 0.3*M*) into the exit stream of the mixing tank (upstream from the sludge bed), so that the final concentrations of NaOH and Na_2CO_3 in the feed stream to the sludge bed would be 0.005*M*. The simultaneous addition of the precipitation-inducing reagents was carried out by adding all reagents to the mixing tank.

The findings of the sludge-bed column runs confirmed those of the beaker tests in that the separate addition of the reagents was again shown to improve phosphate removal. The residual total hardness was less (even after 7 hr) when the precipitation-inducing reagents were added separately than when they were added simultaneously (see Fig. IV-7). Thus the adding of reagents separately is of value for LAW

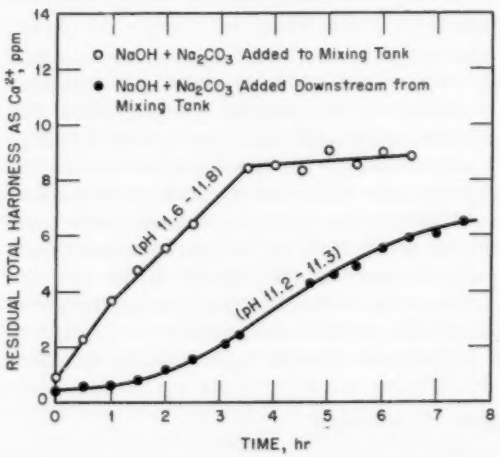
o NaOH + Na_2CO_3 Added to Mixing Tank
• NaOH + Na_2CO_3 Added Downstream from Mixing Tank
(pH 11.6 - 11.8)
(pH 11.2 - 11.3)
RESIDUAL TOTAL HARDNESS AS Ca^{2+}, ppm
TIME, hr

Fig. IV-7 Changing the caustic-carbonate addition point can reduce the deleterious effects of phosphate on hardness removal.[7]

streams containing high concentrations of phosphate (5 to 15 ppm), provided that the periods of high concentration are only of a few hours' duration. However, for a prolonged period of high phosphate content in the LAW, there would be little difference in the results of separate or simultaneous addition of precipitation-inducing reagents, since an equilibrium between precipitated ferric phosphate and hydrous ferric oxide would eventually be reached.

ORNL is continuing its plans for a pilot-plant demonstration of the foam-separation technique.[11] Foam-separation equipment (see Fig. IV-8) is being designed for installation in the Low-Level-Waste Pilot Plant.[7] The equipment will include a countercurrent foam column (2 ft square by 14 ft high), three recovery columns in series for the removal and recycle of surfactant from the waste effluent before disposal, and two types of foam-breaking equipment. The maximum waste feed rate for the system will be about 5 gal/min. The presently installed sludge clarifiers and filters in the Low-Level Pilot Plant will be used for hardness (calcium and magnesium) removal from the waste solution before it is fed to the countercurrent foam column. Solids-feeding equipment will also be installed for adding grundite clay to the sludge clarifier for cesium removal.

Conversion of High-Level-Activity Wastes to Solids

In the United States, three major calcination processes (fluidized bed, pot calcination, and radiant heat spray) are being developed for the safe ultimate disposal of high-level-activity wastes.[12] Development work on the rotary-ball kiln, as a waste-calcination process, was terminated during fiscal year 1963 because this approach was felt to be more complicated than other promising processes for waste calcination.[13] Other processes under development include direct conversion of waste solutions to

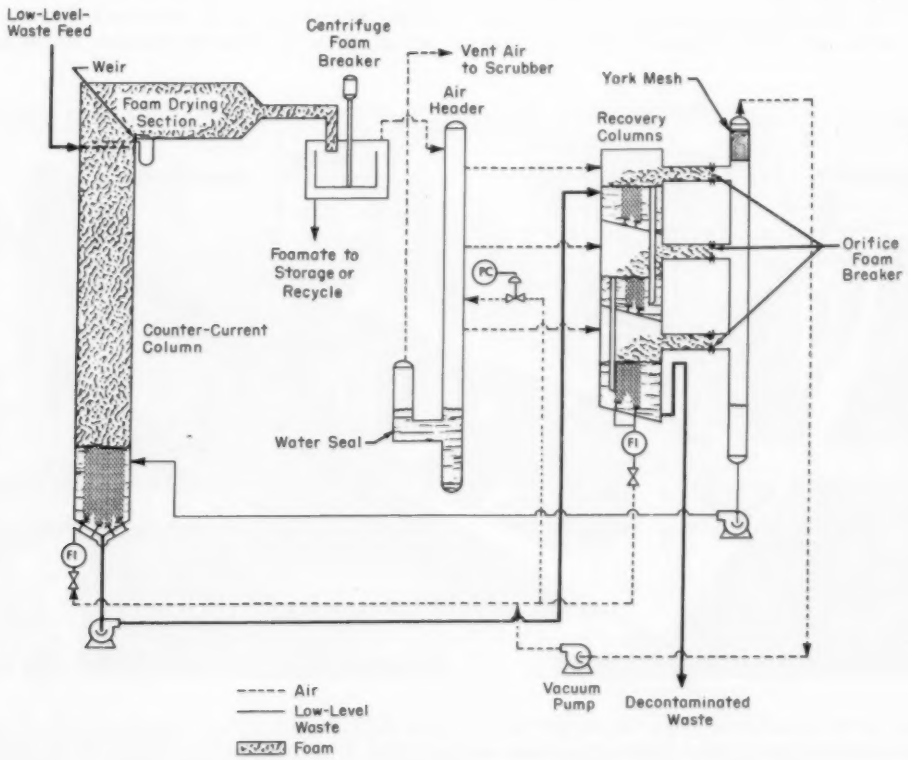

Fig. IV-8 Foam-separation pilot plant.[7]

glasslike compounds,[14] decomposition of waste and fixation of the metallic salts therein in molten sulfur,[15,16] and adsorption of radioactivity in solutions on clay type minerals followed by high temperature calcination.[16]

Fluid-Bed Calcination

A demonstration of the fluid-bed calcination of high-level-activity liquid wastes is currently being carried out in the Waste Calcining Facility (WCF) at the National Reactor Testing Station.[12] A cutaway sketch[17] of the WCF and its principal equipment is shown in Fig. IV-9. Buckham and associates[17] have presented data on the initial two months of operation of the WCF with radioactive wastes. An overall material balance for this initial period of operation is given in Fig. IV-10. It shows that essentially all the solids and radioisotopes from the raw feed to the calciner were to be found in the combined product, which is sent to the storage bins, and that only a very small portion of the combined product passed through the final filters with the final process off-gas to the stack. The performance of the off-gas cleanup system was considered to be excellent during the initial period of radioactive operation. Average decontamination factors for three of the principal radionuclides (^{137}Cs, ^{90}Sr, and ^{106}Ru) for each of the major components[18] (see Fig. IV-11) of the off-gas system are shown in Table IV-2. The ^{137}Cs and ^{90}Sr, which are entrained along with solids in the off-gas, were removed in each component to approximately the same degree, with an overall decontamination factor (beyond the high-efficiency filters) for these isotopes of almost 10^7. The major amount of the ^{106}Ru, which is present in the process off-gas largely as a volatile compound (RuO_4), is removed by the silica adsorbers. The overall decontamination factor for the ruthenium amounted to 1800, which is considered satisfactory.

In the calciner vessel at the WCF, the bed of alumina particles (~0.5 to 0.6 mm mean diameter) is fluidized by preheated air that is distributed uniformly to the bed by means of an air-distributor plate (Fig. IV-12) containing 14 equally spaced orifices. Each orifice is surmounted by a cap that helps to minimize bed attrition caused by particles being struck by the high velocity of the air from the orifice. The cap also helps to minimize the backflow of solids into the plenum chamber of the calciner

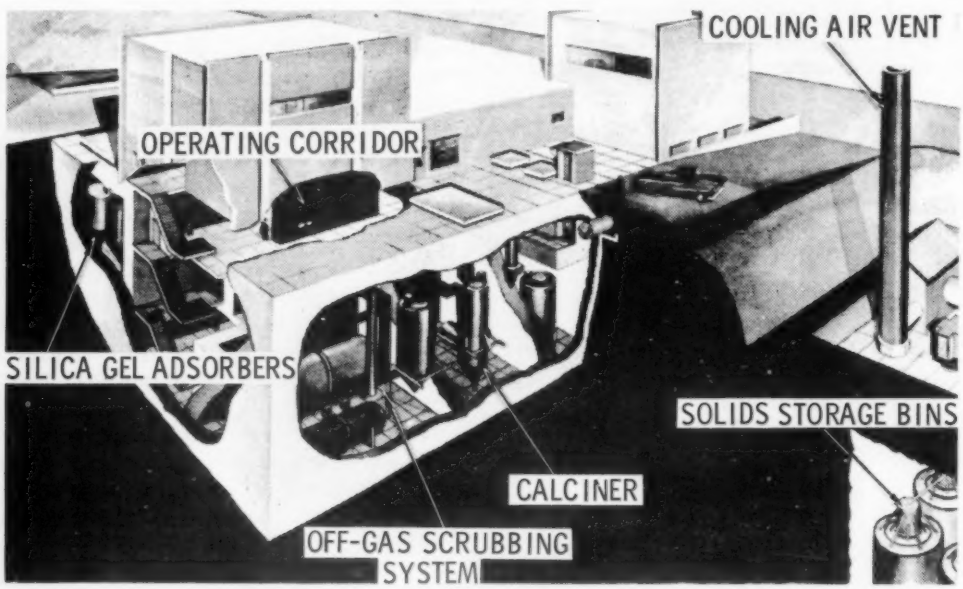

Fig. IV-9 Cutaway sketch of the waste-calcining facility.[17] *(Reprinted from a paper.* Fluidized-Bed Calcination of High-Level Radioactive Waste in Plant Scale Facility, *presented by J. A. Buckham, A. L. Ayers, and J. A. McBride at the 53rd National Meeting of the A.I.Ch.E., Pittsburgh, Pa., May 17–20, 1964, by permission from the American Institute of Chemical Engineers.)*

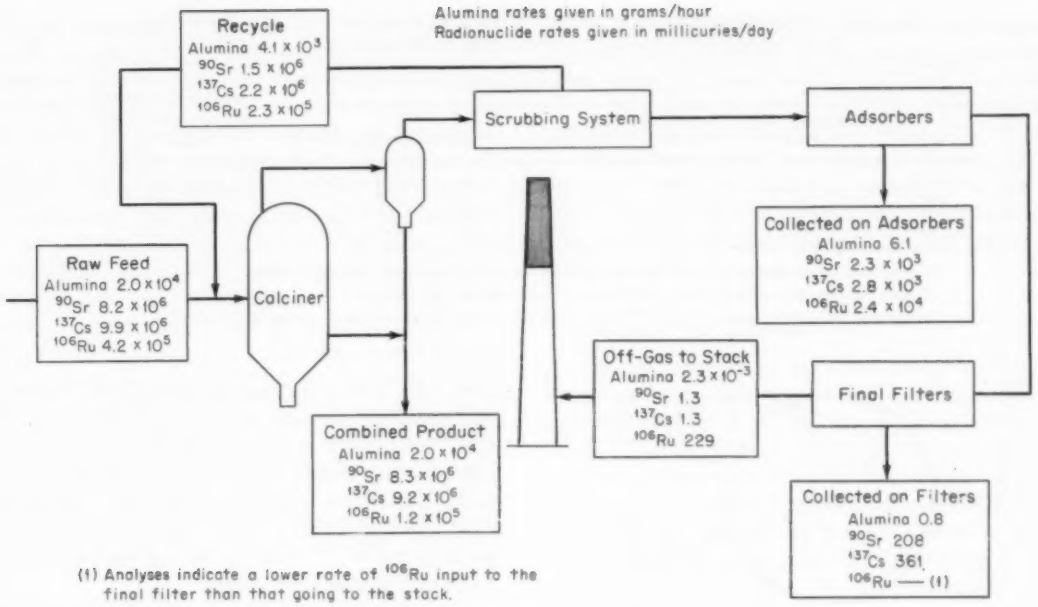

Fig. IV-10 Waste-calcining facility solids and radionuclide balance.[17] (Reprinted from a paper, Fluidized-Bed Calcination of High-Level Radioactive Waste in Plant Scale Facility, *presented by J. A. Buckham, A. L. Ayers, and J. A. McBride at the 53rd National Meeting of the A.I.Ch.E., Pittsburgh, Pa., May 17–20, 1964, by permission from the American Institute of Chemical Engineers.)*

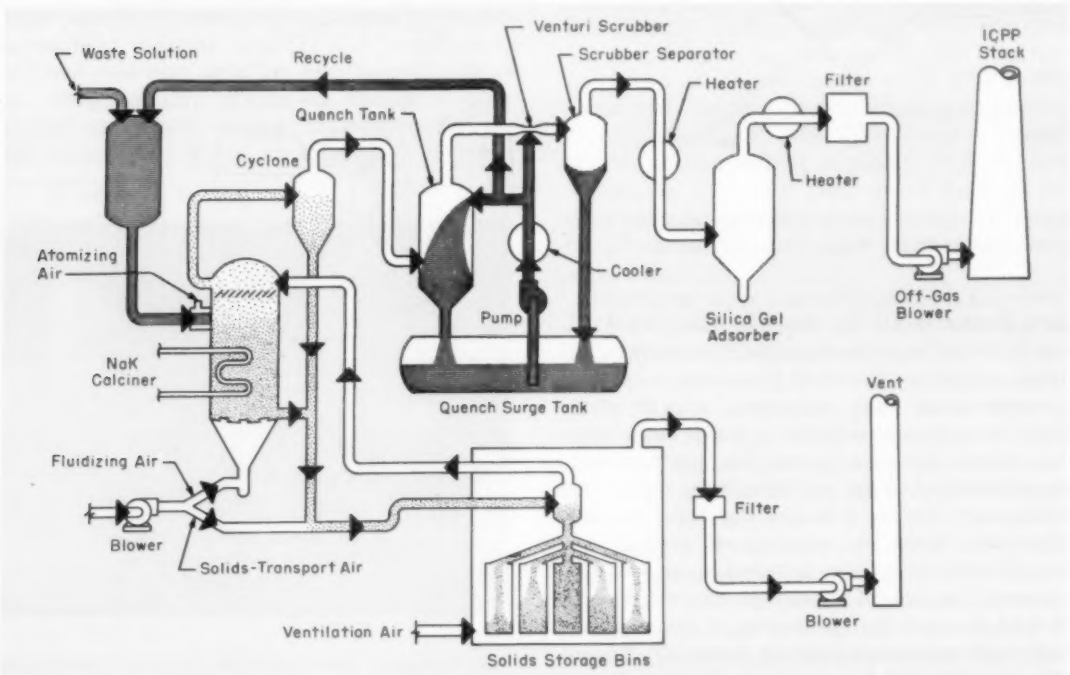

Fig. IV-11 Schematic flow sheet of fluidized-bed waste-calcining facility.[18]

Table IV-2 DECONTAMINATION FACTORS* FOR PRINCIPAL NUCLIDES DURING INITIAL WASTE-CALCINING FACILITY OPERATION WITH RADIOACTIVE FEED[17]

Nuclide	Component performance†					Overall performance of process, raw feed to stack
	Calciner and cyclone	Scrubbing system	Adsorbers	Filters	Composite	
^{137}Cs	6.0	690	9	280	10×10^6	7.6×10^6
^{90}Sr	6.5	600	12	160	7.5×10^6	6.3×10^6
^{106}Ru	2.5	11	410	‡	2.8×10^3	1.8×10^3

*Decontamination factor = (radioisotope influent rate)/(radioisotope effluent rate).
†Based on contents of feed tank, including recycled scrubbing solution.
‡Analyses indicate a lower rate of ^{106}Ru input to the final filters than that going to the stack.

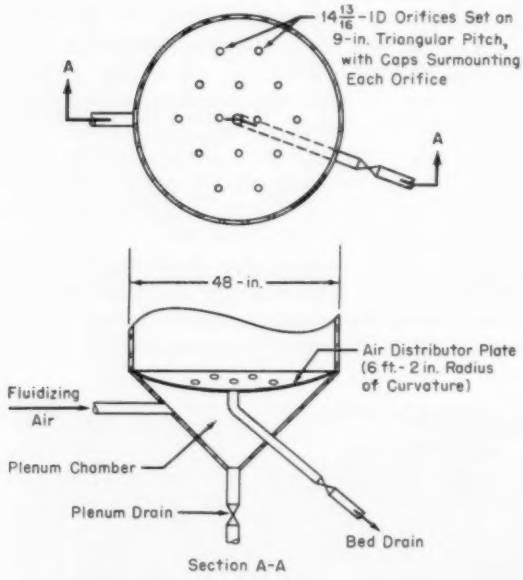
14 13/16 - ID Orifices Set on 9-in. Triangular Pitch, with Caps Surmounting Each Orifice
A
A
48 - in.
Air Distributor Plate (6 ft - 2 in. Radius of Curvature)
Fluidizing Air
Plenum Chamber
Plenum Drain
Bed Drain
Section A-A

Fig. IV-12 Location of air-distributor plate and caps in the calciner at the Waste Calcining Facility.[19]

when fluidizing air is stopped. When the WCF was in operation with nonradioactive waste solutions, excessive erosion of the original installed air-distributor caps occurred. A pilot-plant study[19] was then undertaken in which the factors that affect the erosion and the performance characteristics of the air-distributor caps were determined. On the basis of the results of the pilot-plant tests, a satisfactory design (see Fig. IV-13) for an air-distributor cap was developed. The use of a plate-to-cap separation of 0.12 in., and the elimination of obstructions in the path of the high-velocity (160 to 200 ft/sec) air emerging from underneath the distributor cap were shown to minimize both countercurrent diffusion (with consequent erosion) of alumina-bed particles beneath the cap and particle attrition. The newly designed distributor caps were successfully tested (no obvious signs of erosion were observed) in the WCF calciner during the final cold shakedown run. They are now being used in the WCF calciner during operation with radioactive waste solutions.

The granular calcined product (alumina) resulting from the fluid-bed calcination of the liquid wastes at the WCF is being stored in underground storage bins[12] (see Figs. IV-9 and

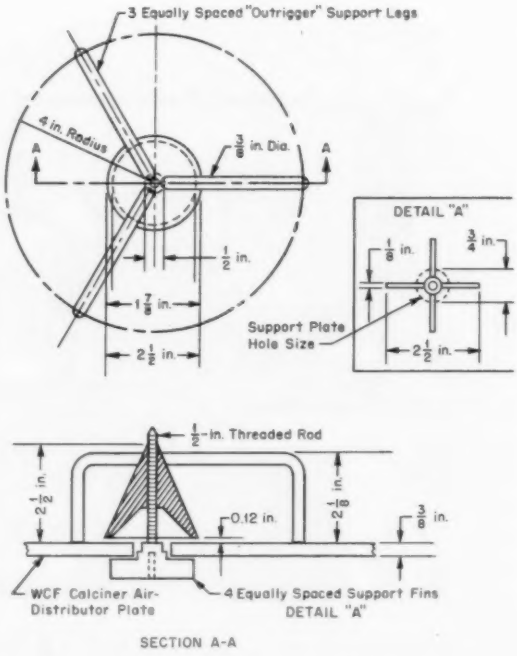

Fig. IV-13 Modified air-distributor cap for fluid-bed calciner.[19]

IV-11). Although only bin type storage at the ICPP is currently being considered[20] for the calcined alumina, at some future date it may be necessary to convert the calcined alumina from the WCF to a glass to achieve an additional degree of safety during long-term storage. A study[21] has been undertaken at the ICPP which investigated the conversion of the calcined alumina from the WCF to a vitreous form for permanent storage. In initial work using nonradioactive calcined alumina from a WCF cold demonstration run, glass specimens were prepared which had the following composition: P_2O_5 (40.5 wt.%), Al_2O_3 (25 wt.%), Na_2O (18.6 wt.%), and PbO (15.9 wt.%). (This glass composition was selected on the basis of previous work[22] conducted at ORNL in which a glass with satisfactory physical properties was produced from aluminum nitrate solutions.) Glasses were prepared by the stepwise heating (400, 570, and 920°C—the fusion temperature) of mixtures of sodium monobasic phosphate, lead oxide, and calcined alumina solids. Molds of platinum or nickel were used with Aquadag as the mold release. Figure IV-14 shows specimens of the glasses that were prepared. (Fusion in platinum produced the gray discoloration seen in the lower specimen.) The specimens contained no cavitations and were homogeneous except for small amounts of residual sand that were contained in the bed material used for startup operation of the WCF. Molded specimens that were slow cooled for annealing had little or no stress. Specimens that were air quenched at room temperature contained stresses that sometimes caused disintegration of the shaped specimen. The glass produced has a density of 3.0 g/cm^3. The reduction in waste volume produced by calcining to alumina in the WCF was ~10.2, whereas there was an increase in volume of about 1.3 when alumina was converted to glass. This results in an overall volume reduction that is similar to the range of 7.2 to 8.4 reported for direct vitrification.[21]

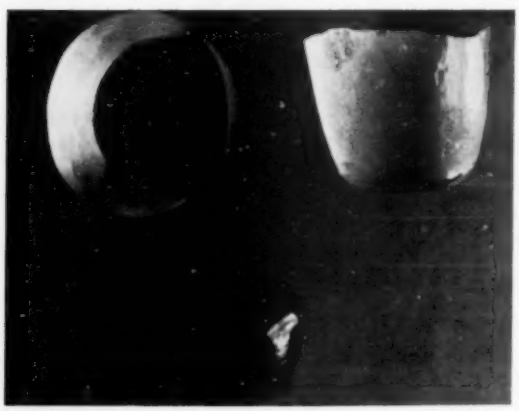

Fig. IV-14 Glasses prepared from calcined alumina.[21] (Courtesy of Atomic Energy Division, Phillips Petroleum Co., Idaho Falls, Idaho.)

Conversion to Glasses

Work is continuing at ORNL on the development of a process for converting high-level-activity wastes to solids. The process is based on combining glass-forming additives with the waste for subsequent formation of a glasslike material in which the fission products are fixed.[23] Two methods are being studied.[7] The first method involves evaporating the plant waste containing added glass-forming materials and then feeding the concentrated waste to a calciner, which is operated with a rising liquid level, for final calcining and melting to a glass. The calciner pot also serves as the final storage container. The second method is a horizontal, continuous melt system in which the plant waste containing the added glass-forming materials is fed directly into a horizontal melt vessel in which the waste is converted directly (without an intermediate calcination step) to a molten glass that can flow to and solidify in the final storage container. The outstanding advantage of the second method is that it is a one-step continuous operation from plant waste to the final storage container. Both methods are being tested in laboratory- and engineering-scale experiments.

Two tests were conducted of the rising-level method of calciner pot operation, utilizing an 8-in.-diameter vertical calciner pot in conjunction with an evaporator. In both tests, simulated TBP-25 waste containing added NaH_2PO_4 ($2M$) and $Pb(NO_3)_2$ ($0.25M$) for glass formers was used. In the first test an operational limitation was imposed in that not over 1 ft of liquid (over the solids formed) was to be present in the calciner at one time. After a period of calciner operation at a feed rate of 10 to 12 liters/hr, the off-gas line became severely plugged, resulting in temporary interruption of the test in order to clean the off-gas line. The test was then continued at a reduced calciner feed rate (6 to 7 liters/hr). During the remainder

of the run, it was necessary to backflush the off-gas line with nitric acid because of plugs that had started to form a number of times. At the end of the test, the off-gas line was found to contain a brown calcined substance that appeared to be calcined foam. In the calciner pot about 90% of the solid was in the form of a very hard, green-colored glasslike substance. There were a number of nonhomogeneous areas in the glass. The bottom area contained a large number of lead globules; other areas contained nonmelted, calcined-solids inclusions. After removal of the solids from the calciner pot, the pot was sandblasted and examined for corrosion pitting. Some pits as deep as 150 mils (initial wall thickness, 350 mils) were found. The bottom 2 ft of the thermocouple well and thermocouples were completely disintegrated.

In the second test, the average calciner feed rate was ~5 liters/hr. The operating procedure was to allow only one heat zone (1 ft in length) of the calciner to be filled with feed at one time. The resulting glass solid was fairly homogeneous in appearance but had areas of included calcined solid and metallic lead. The glass had a residual nitrate content of 370 ppm and a bulk density of 2.24 g/cm^3.

For testing of the continuous melting system, the horizontal melt vessel shown in Fig. IV-15 was used. It is constructed of 304L stainless steel (350 mils thick) and is 40 in. long, with a 36-in. feeding zone. The melt vessel is heated by a 25-kw resistance furnace having four temperature-controlled zones. A baffle located at 4 in. from one end extends 2 in. under the normal melt level, acting as a skimmer to remove floating solids and allowing only melt to enter into the overflow line. The molten-glass product is withdrawn through a baffled freeze-trap valve (see Fig. IV-16). Along the bottom of the melt vessel are five $\frac{1}{4}$-in.-diameter stainless-steel lines that are placed at equal intervals for sparging (with nitrogen) the melting glass. The process off-gas is removed through a 2-in.-diameter line (see Fig. IV-17) that is also equipped with a glass port for viewing the feed nozzles and the solids in the melt zone.

A preliminary test of the horizontal melt vessel was carried out with a simulated TBP-25 waste containing 2 M Na_2HPO_4 and 0.25 M $Pb(NO_3)_2$ for glass formers at feed flow rates up to 20 liters/hr. This mixture forms a calcined solid between 400 and 600°C and melts at about 750

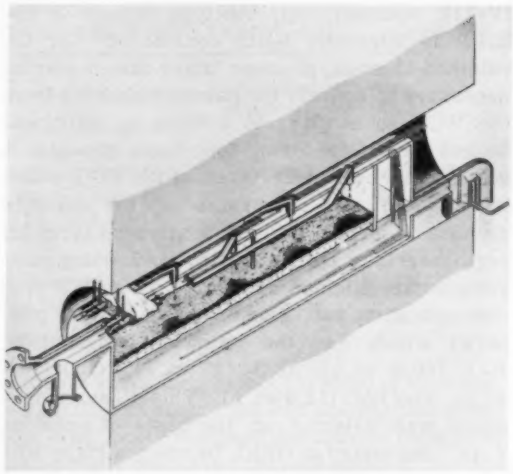

Fig. IV-15 High-level-waste continuous melter.[7]

to 800°C. At 850 to 900°C, it is sufficiently fluid to be removed from the horizontal melt vessel by gravity flow. The test was considered a success. The simulated TBP waste (with added glass formers) was evaporated on the surface of a shallow pool of molten glass that flowed continuously from the vessel. There was no evidence of corrosion in the horizontal melt vessel, although it had been operated for some 15 days at temperatures that ranged from 600 to 1000°C. (In preliminary experiments to form glasses from simulated TBP and Purex wastes in vertical melt pots, extreme corrosion was observed in the areas where lines were brought into the melt pot beneath the melt level. As a result, the horizontal vessel was designed without any lines penetrating the vessel below the glass-melt level.)

A horizontal melt vessel of an alternative design (see Fig. IV-18) is being built for testing with simulated Purex and TBP-25 aqueous wastes.[7] An agitator was added to improve heat transfer to the evaporating wastes by preventing the buildup of a layer of deposited solids (cake) on the wall above the liquid level.

Pot Calcination

At ORNL, a pot-calcination process is being studied for converting high-level-activity wastes to solids.[7,24] In this process the wastes are first evaporated and then calcined to solids in cylindrical stainless-steel pots that, when weld

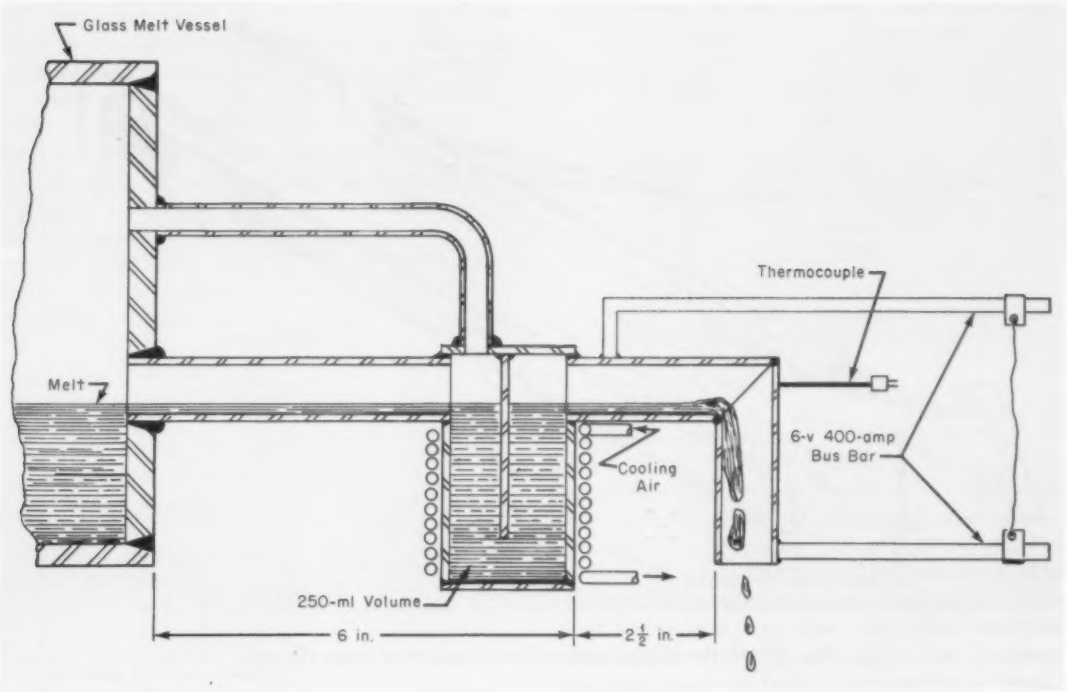

Fig. IV-16 Baffled-trap freeze valve.[7]

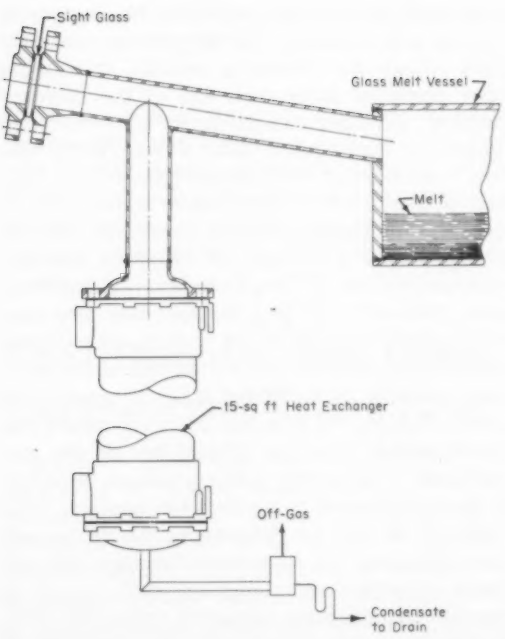

Fig. IV-17 Off-gas removal system.[7]

sealed, serve as the final storage container. As part of the investigation of the calcination process, the behavior of mercury that is present in TBP and Purex-plant wastes is being studied. Mercury is not retained by the calcined solid product because its compounds are unstable at the high temperatures (about 900°C) of the process. Cyclone traps[25] have been partially successful in removing (up to ~50%) the volatilized mercury from the calciner off-gas stream. However, a pretreatment method has been developed for removing the mercury directly from the waste solution. It involves forming a mercury amalgam[7,25,26] with an active metal (e.g., copper or aluminum), which is accomplished by passing the waste solution through a column containing the active metal. A batch or continuous operation may be carried out. In the batch operation the column (and the contained mercury amalgam that has formed) is discarded upon breakthrough. In the continuous operation (see Fig. IV-19), the amalgam that is formed is removed at the bottom of the column. The active metal, as it is needed, is added through the top of the column. Laboratory ex-

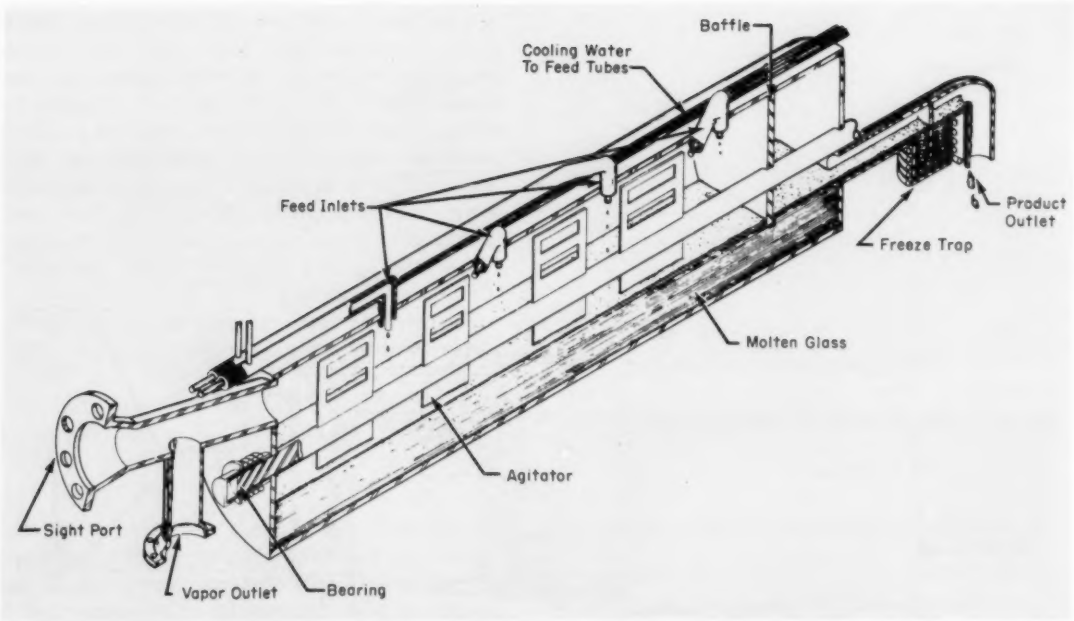

Fig. IV-18 Horizontal, agitated melt vessel for waste fixation.[7]

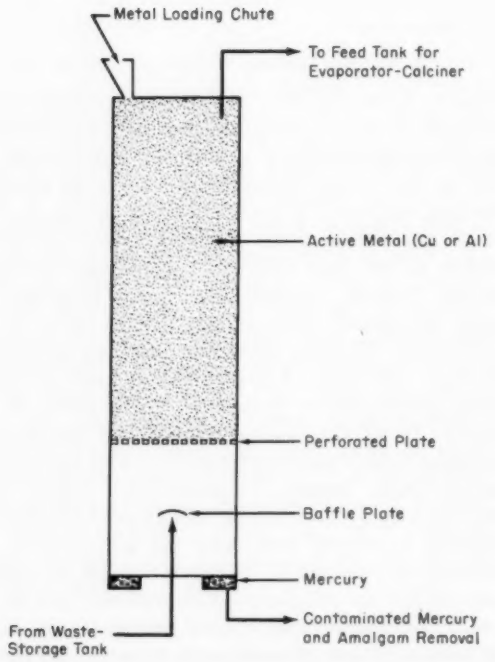

Fig. IV-19 Schematic diagram of proposed column for continuous removal of mercury from acid waste solutions.[7]

periments have been carried out in which various column-packing materials have been tested for their ability to remove mercury from simulated plant-waste solutions. The tests with copper and aluminum as the packing material have shown the following results. (1) Copper shot removed more than 99% of the mercury present in simulated Hanford FTW-65 plant waste (a Purex-plant acid waste (1WW) that has been treated with formaldehyde to reduce the nitric acid concentration from ~6*M* to ~0.5*M*). Anodization (anodic current of 120 ma) of the copper prolonged its effective life as a bed material for FTW-65 wastes. It is questionable, however, whether the increase warrants the added complexity of design. (2) Copper effectively removed more than 99% of the mercury present in simulated TBP-25 waste (acid concentration, ~1.3*M*), but so much copper was found dissolved in the effluent that its use may not prove to be econon ically practical. However, it may be possible to remove the mercury from TBP-25 wastes by decreasing the nitric acid concentration. (3) Aluminum turnings (the only form investigated; aluminum shot should be equally satisfactory) removed some 98% of the mercury present in a simulated Hanford FTW-65 plant waste that had been threefold concentrated

(acid concentration, ~1.5*M*). (4) Neither aluminum nor copper was effective in removing mercury from simulated Purex 1WW waste (acid concentration, ~5.6*M*). Both metals were attacked rapidly by the relatively concentrated nitric acid in the waste solution. Removal of the mercury from this waste by the mercury-amalgam method would require a decrease in the high acid concentration.

A proposed flow sheet for the continuous removal of mercury from low-acid plant-waste solutions is shown in Fig. IV-20. The column

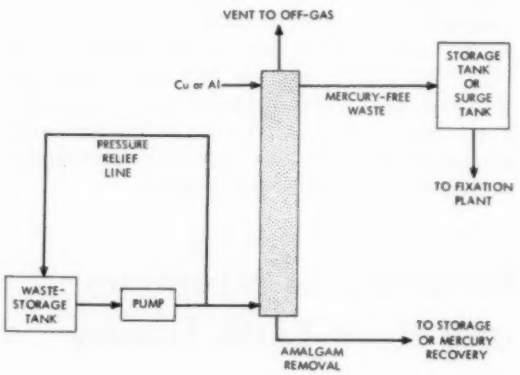

Fig. IV-20 Proposed flow sheet for removal of mercury from low-acid waste solutions by displacement with copper or aluminum.[26]

containing either copper or aluminum is placed between the waste-storage tank and the feed tank for the fixation process. Vibration of the packed column may be helpful in ensuring proper packing of the bed to prevent channeling and plugging and to facilitate mercury-amalgam removal.

Final Disposal into Deep Impermeable Formations

Savannah River has been investigating the feasibility of storing long-cooled radioactive wastes from its fuel-separations facilities in chambers excavated in the basement rock beneath the plant.[27,28] In a typical processing-plant waste that has been stored for some eight years in surface-buried tanks for the decay of the shorter-lived isotopes, the major constituents are:

Constituent	Concentration*
$NaNO_3$	3*M* to 4*M*
Na_2CO_3	0.3*M*
Na_2SO_4	0.2*M*
NaOH	0.3*M*
$NaAlO_2$	0.6*M*
^{90}Sr	0.1 to 10 curies/gal
^{137}Cs	0.1 to 10 curies/gal
Plutonium	Trace
Neptunium	Trace

*Differences in composition resulting from the solution separating into a sludge layer and a supernatant liquid are not considered.

Of the radioactive isotopes present in the aged waste, ^{90}Sr is the limiting fission product because of its 28-year half-life, relatively high concentration in the waste, and very low Radioactivity Concentration[29] Guide* (RCG) concentration (1×10^{-7} μc/ml). The half-lives of the actinide elements, such as neptunium, plutonium, and americium, are also very long, and their RCG concentrations are quite low. However, because these materials are insoluble, the actinides under most conditions migrate through the ground only at very low rates compared with strontium and cesium.[31] Next to ^{90}Sr, the most hazardous fission product in the aged waste is ^{137}Cs, with a half-life of 30 years. However, since ^{137}Cs has an RCG concentration about 200 times higher than that of ^{90}Sr, the same concentration of cesium is about 200 times less hazardous. In addition, under most conditions in soils, cesium adsorbs more readily than does strontium and thus migrates more slowly.

The wastes stored at Savannah River are alkaline and consist of two fractions, a supernatant liquid containing nearly all the cesium and very little of the strontium and a sludge containing nearly all the strontium, probably as an insoluble carbonate. Because the rock walls of a storage chamber can react with either an alkaline or an acid waste to form a nearly neutral solution, no reliance is placed on keeping the strontium insoluble. Therefore after several years' storage, the strontium is assumed to be

*"Radioactivity Concentration Guide" is defined as the concentration of radioactivity in the environment which will result in whole body or organ doses equal to the Radiation Protection Guide.[30]

in solution as the bicarbonate. About 600 years is required for the ^{90}Sr in the waste to decay to innocuous levels.

As part of this program, the ground beneath a 3-sq mile area at Savannah River was explored to determine the attitude, continuity, types, and character of the basement rock underlying the area. These studies show that radioactive waste solutions can be stored safely, without hazard to the on-site or off-site environs, in storage chambers excavated in the basement rock 1300 to 1700 ft underground beneath the plant. Storage of liquid radioactive wastes in such chambers is technically feasible because:

1. The physical and chemical properties of the basement rock place no unusual restrictions on the construction of the chambers.
2. The hydrologic conditions of the basement rock and the overburden would isolate any wastes that might escape the chambers.
3. Seismic disturbances are unlikely to damage the chambers.

A conceptual design (see Fig. IV-21) has been developed for a 20-million-gal storage facility, consisting of four 5-million-gal storage chambers constructed underground. A concrete-lined main shaft (15 ft in diameter) is provided for construction purposes and for access to the storage level. Each storage chamber is isolated from the main shaft area by two monolithic concrete bulkheads that are designed to withstand the full hydrostatic head that could be developed if the fill lines should fill to the ground surface. The storage chambers are equipped with instruments to transmit data on the liquid levels and temperatures throughout the chambers to the control room at the ground surface. Any inleakage of ground water collected in the storage chamber is pumped out to provide maximum storage capacity at the time that waste is charged to each chamber. The location of each chamber relative to the others is a function of the characteristics of the rock structure, of construction practices, and, to a lesser extent, of the rate of heat transfer from the stored waste to the surrounding rock. Service shafts (18 in. in diameter) from the ground surface to each chamber contain vent and fill lines, electric power and instrument cables, and a sump-pump discharge line.

The construction cost is estimated to be $12.5 million. Based on this cost alone, the unit cost per gallon of stored waste is $0.625. If the size of the initial storage facility were increased to 40 million gal, the approximate unit cost per gallon would be $0.36.

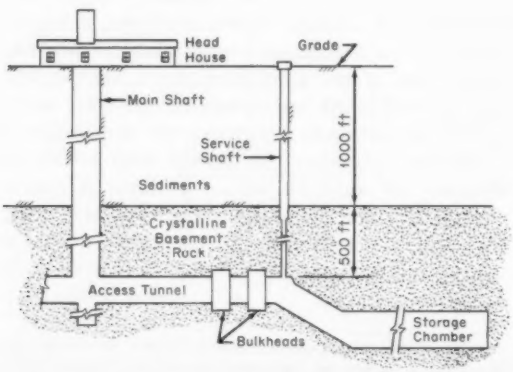

Fig. IV-21 Cross section of storage facility.[28]

Recovery of Strontium and Rare-Earth Fission Products

Yee and Davis[32] have reported on work being carried out at ORNL for the cation-exchange recovery of strontium and/or rare earths from Purex-plant acid waste (1WW).[33] Major cationic impurities (iron, chromium, and aluminum) present in the 1WW greatly interfere with the ion-exchange separation of strontium and rare-earth elements from this solution. In addition, the presence of sulfate ion in the 1WW prevents the use of precipitation as a means of separating strontium as the nitrate from these impurities. The authors[32] have described two proposed methods for the head-end treatment of 1WW prior to subsequent processing by ion exchange for the recovery of strontium and/or rare earths. One method (see Fig. IV-22) involves complexing of the major cationic impurities with citrate ion at *p*H 2.5 and processing of the resulting waste solution that has been diluted 20-fold through a column of resin (Dowex 50W in the ammonia form) where the uncomplexed strontium and rare-earth elements are sorbed. Laboratory tests of this pretreatment method, with simulated 1WW and subsequent ion-exchange processing of the 20-fold-diluted, pre-

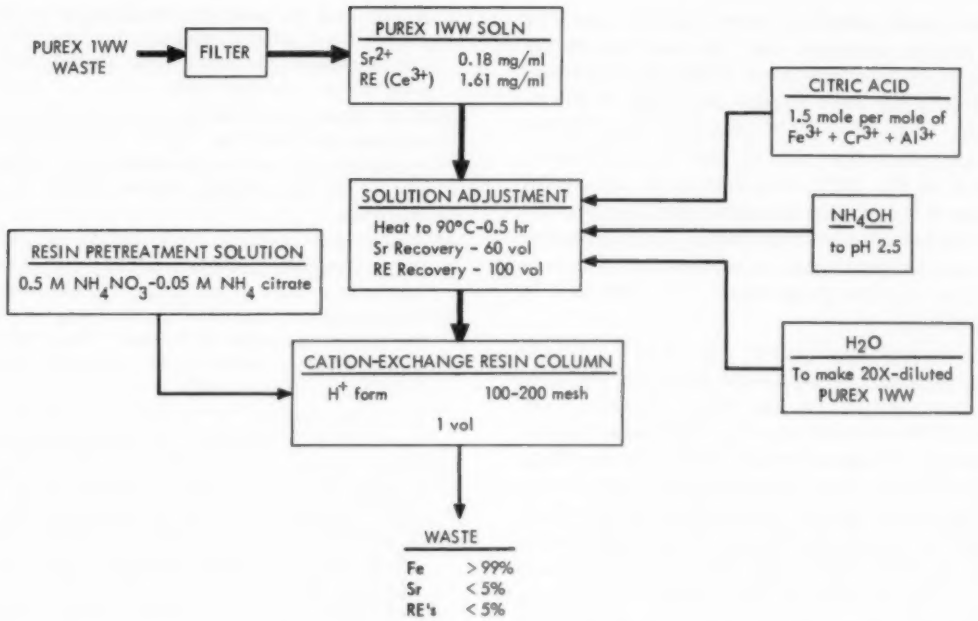

Fig. IV-22 In this flow sheet, the trivalent cationic impurities (Fe^{3+}, Cr^{3+}, and Al^{3+}), after being complexed with citrate, pass through the ion-exchange column while strontium and rare-earth cations are sorbed on the resin.[32]

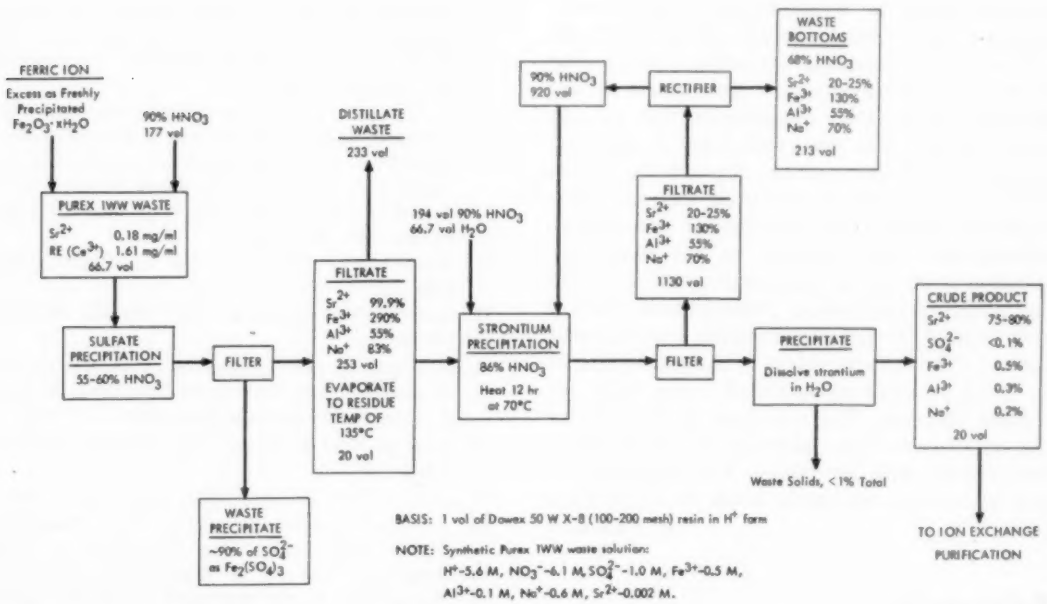

Fig. IV-23 In this flow sheet,[32] *first sulfate is removed by precipitation from simulated Purex 1WW waste as $Fe_2(SO_4)_3$ from 55 to 60% HNO_3, and then $Sr(NO_3)_2$ is recovered by precipitation from 85% HNO_3.*

treated waste solution, were carried out. The test results indicated that the capacity of the cation resin was increased 3-fold for strontium and 4-fold for rare earths over that of an untreated, simulated 1WW that had been diluted 10-fold. Less than 1% of the iron originally present in the 1WW was sorbed on the resin. Elution of the sorbed strontium and rare earths was conducted with ammonium α-hydroxyisobutyrate. Decontamination factors for strontium and rare earths from iron were 600 and 5, respectively.

The second method (see Fig. IV-23) consists in a two-step precipitation process: (1) precipitating sulfate ion (as ferric sulfate) from Purex 1WW waste at 55 to 60% HNO_3 and (2) precipitating strontium nitrate from the resulting nearly sulfate-free solution from 86% HNO_3. The strontium nitrate precipitate is then dissolved for subsequent removal and purification of the strontium by means of a cation-exchange resin (Dowex 50W in the ammonium form). Laboratory tests of pretreatment by the double-precipitation method were performed with simulated Purex 1WW. The results showed that the strontium was concentrated by a factor of 2.5 to 3.0 and that the ratio of total trivalent cationic impurities to strontium was reduced by more than 200. When the strontium nitrate precipitate is dissolved in a minimum amount of water, the volume of the resulting strontium concentrate solution is about one-third the volume of the original 1WW. This concentrate solution, to which citrate was also added for complexing purposes, was then passed through the cation resin for sorption of strontium that was subsequently eluted with ammonium α-hydroxyisobutyrate. The capacity of the resin for sorption of strontium was improved 20-fold with the double-precipitation pretreatment method over that of the citrate-complex pretreatment method. This is equivalent to the processing of up to 67 volumes of undiluted Purex 1WW per volume of resin. The recovery of rare earths was not improved, because they are only partially precipitated with strontium. The decontamination factor for strontium from iron amounted to 5×10^5. (P. Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Application of Fluidization Techniques to Uranium Processing

Gas-solid reactions, particularly the reduction of uranium trioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important in the production of both uranium metal and uranium hexafluoride. The rate of these reactions is determined by the structure of the solid surface which, in turn, is modified during the progress of the reactions. Because thermal damage of the solid surface is significant in this type of heterogeneous reaction, considerable attention has been directed toward using fluid-bed reactors in the production of uranium feed materials. Fluid-bed reactors offer the advantage of efficient gas-solid contact and temperature control.

Fluid-Bed Processing at Springfields

Lloyd,[1] in an article on gas-solid contacting, has described the application of fluidization techniques to the production of uranium tetrafluoride at the Springfields Works of the UKAEA. The processing sequence at Springfields involves the thermal decomposition of uranyl nitrate to produce free-flowing UO_3 powder, the reduction of UO_3 to UO_2, and the hydrofluorination of UO_2 to UF_4. Each process step is carried out in fluid-bed equipment. The conversion of uranyl nitrate solution to uranium trioxide is effected by atomizing the uranyl nitrate solution into a bed of UO_3 that is fluidized with air and maintained at a temperature of 350°C. The primary heating system for the fluid-bed reactor consists of electric heaters which are enclosed in stainless-steel tubes and which are immersed in the fluid bed. Auxiliary heat is supplied by external resistance heating elements. Uranyl nitrate feed is introduced to the reactor through a system of six atomizers located on the periphery of the reactor at a fixed position below the fluid-bed level. The nitrous gases leaving the reactor are filtered through a bank of sintered stainless-steel filters and fed to an absorption unit for the recovery of nitric acid. The UO_3 product is continuously removed from the bottom of the fluid-bed reactor and pneumatically conveyed to a storage hopper.

Both the reduction of UO_3 to UO_2 with hydrogen and the hydrofluorination of UO_2 to produce UF_4 are conducted in fluid-bed reactors on a batch operation. Since the reactions are carried out on a batch basis, both heating and cooling facilities are provided for each reactor. At the start of the reaction, heat is supplied to the vessel by electric heating elements externally mounted on the reactor shell. At the end of the cycle, cooling is provided by forced air, directed over the vessel wall by fins located in channels between the heating elements. Each reactor is provided with facilities for filtration of the off-gases, for heat exchange between inlet and outlet gases, and for recirculation or recovery of excess reagents.

On May 17–20, 1964, the American Institute of Chemical Engineers sponsored a symposium on nuclear plant experience with fluidized beds.[2] In a review article, Blocher and associates[2f] discussed the application of fluidization techniques to the production of nuclear fuel materials.

Processing of Uranium Ore Concentrates

Sutton and associates[2a] have described the operation of the uranium feed-materials plant at Metropolis, Ill., with particular emphasis on the description of the reduction and hydrofluorination processing steps. This plant, operated

by the General Chemical Division of Allied Chemical Corporation, converts ore concentrates to uranium hexafluoride by hydrogen reduction, hydrofluorination, and fluorination in fluidized-bed reactors. A detailed description of the process used at the Metropolis plant was reported in a previous issue of *Reactor Fuel Processing*.[3]

Ore concentrates, assaying about 70% U_3O_8, are extruded into pellets, dried, and crushed to give −40 +200 mesh particles suitable for feed to the fluid-bed reactors.[2a] The reduction of the concentrate to UO_2 is carried out in a single-stage fluid-bed reactor at temperatures between 540 and 600°C. The fluidizing gas is a mixture of hydrogen and nitrogen prepared by the catalytic dissociation of ammonia at 900°C. The reduction reactor is constructed of $\frac{5}{8}$-in.-thick type 304 stainless steel. The reactor is $14\frac{1}{2}$ ft in height above the gas-distribution plate. The diameter of the vessel increases from 3 ft 1 in. at the distributor plate to 4 ft 6 in. at a height 5 ft 10 in. above the plate. The tapered section is equipped with external, vertical heat-transfer fins. The reduction reactor is operated with continuous solids feed and product discharge. The ore concentrate is fed to the reactor through a rotary valve on a ribbon-screw conveyor. The UO_2 product is discharged by gravity from the bottom of the bed through a vertical leg and rotary feeder to a conveyor serving the hydrofluorination reactors. The reduction reactor has been operated with solid throughput rates as high as 3500 lb/hr and reduction efficiencies of 99%.

Conversion of UO_2 to UF_4 is carried out in two fluid-bed hydrofluorination reactors operated in series with countercurrent solids and gas flow.[2a] The hydrofluorination reactors are constructed of $\frac{1}{2}$-in.-thick Inconel and are essentially identical in design to the reduction reactor. Crude UO_2 is fed directly to the primary hydrofluorinator, where 65 to 70% conversion to uranium tetrafluoride takes place. The partially converted product is continuously withdrawn to the secondary reactor, where the conversion is completed by reaction with anhydrous hydrogen fluoride. Preheated hydrogen fluoride, containing an inert gas to supplement fluidization, is introduced to the secondary hydrofluorinator. It passes countercurrently through the bed and exits at the top of the reactor. The gas stream is filtered through porous carbon filters before entering the primary reactor. The flow rate of hydrogen fluoride is regulated to provide a 10% excess based on the feed rate of UO_2 and to maintain 30 to 35% unreacted oxide in the primary reactor. Both fluid-bed hydrofluorination reactors operate within a temperature range of 455 to 510°C. The conversion of UO_2 to UF_4 in the primary reactor is limited to 70%. Limiting of the conversion permits the heat of reaction per unit bed volume to be limited, and the possibility of sintering UF_4 particles is avoided.

Stirred Fluid-Bed Reactors

Because uranium tetrafluoride is susceptible to sintering or caking at rather low temperatures, especially when in the form of fine particles, screw reactors have often been employed in the production of UF_4 by hydrofluorination of UO_2. However, the production capacity of screw reactors is significantly less than that available in fluid-bed equipment. Also, the effects of powder reactivity on processing rate are considerably more significant in screw reactors than in fluid-bed reactors. Development work carried out in the Nuclear Division of Union Carbide Corporation[2b] showed that by applying slow-speed, mechanical agitation to the fluid bed, caking of UF_4 particles is virtually eliminated and the benefits associated with fluid-bed operation are retained. On the basis of successful demonstration of this concept, stirred fluid-bed reactors were installed as replacement for a system of ribbon-screw reactors in the production line at the Paducah Gaseous Diffusion Plant in 1961.

Production of UF_4 is carried out in two stirred, fluid-bed reactors operated in series with countercurrent flow of gas and solids.[2b] Design of the reactor and stirrer is shown in Fig. V-1. The bottom of the 30-in.-diameter Inconel reactor is coned and contains an Inconel ball to prevent leakage of powder into the gas-inlet line during shutdown. The product-overflow line is located 5.8 ft above the gas inlet. Powder feed is introduced 1 ft below the bed level. The outer wall of each reactor is vertically finned and jacketed to provide an annulus for cooling air from a forced-air system.

The original stirrer design (Fig. V-1) comprised a center shaft of 4-in.-diameter schedule-80 Inconel pipe onto which were welded radial rods joined with four vertical wall-scraping rods and angled braces. The rods and braces were formed from 1-in.-diameter Inconel pipe.

The stirrer drives were d-c motors capable of developing 7.5 hp at the full speed of 40 rpm.

The initial operation of the stirred fluid-bed system indicated that several modifications in the stirrer design were required.[2b] The load on the stirrer drives was about 120% of the rated current. The stirrer was therefore modified, as shown in Fig. V-1. The number of wall-scraping rods was decreased from four to two, and the diameter of the rods and braces was reduced to $\frac{3}{4}$ in. It was also necessary to reduce the stirrer speed from 40 to 22 rpm.

The performance of the stirred fluid-bed reactors in the production of UF_4 has been satisfactory. The capacity of the system is significantly greater than that achieved with the screw reactors used previously, and the conversions to UF_4 have been higher. The two stirred fluid-bed reactors have consistently produced UF_4 in yields of 94 to 97% at processing rates as high as 21 tons of uranium per day.

Recovery of Fluorine in Fluid-Bed Reactors

At the Paducah Gaseous Diffusion Plant, fluid-bed reactors are used for the recovery of fluorine from process gas streams associated with the manufacture of uranium hexafluoride.[2c] Fluorine recovery is based on the reaction between fluorine and uranium tetrafluoride at temperatures of 370 to 400°C to form uranium hexafluoride and intermediate uranium fluorides (U_2F_9, U_4F_{17}, and UF_5). The recovery system consists of a 27-in.-diameter Monel reactor with a 4.5-ft-deep bed of uranium tetrafluoride.

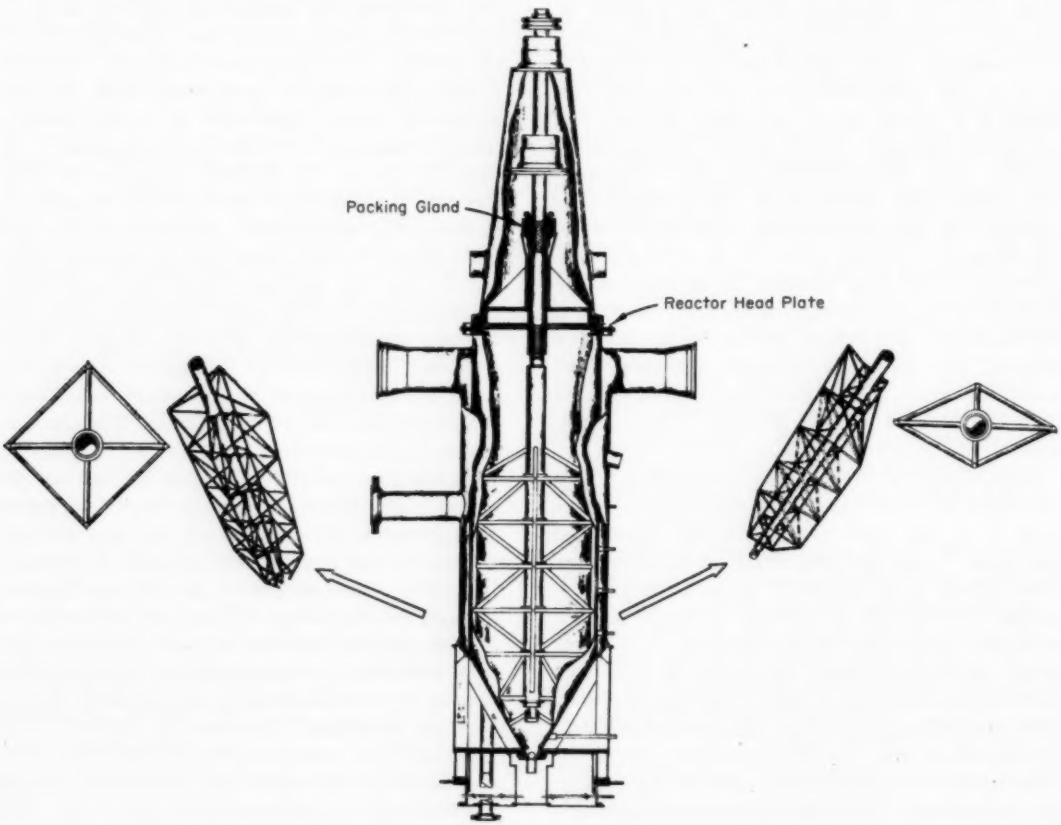

Fig. V-1 Fluid-bed hydrofluorinator reactor. (Reprinted from a paper, Development and Production Experience with Mechanically Agitated Fluid-Beds as Applied to the Hydrofluorination of Fine Uranium Oxide Powders, *presented by D. C. Brater, J. H. Pashley, S. H. Smiley, D. L. Castro, and L. A. Dean at the 53rd National Meeting of the A.I.Ch.E., Pittsburgh, Pa., May 17–20, 1964, by permission from the American Institute of Chemical Engineers.)*

The feed stream for the fluid-bed reactor consists of the primary UF_6 process vent-gas stream and contains from 20 to 40% fluorine. The recovery system has demonstrated an average fluorine-recovery efficiency of greater than 95%. The primary problem in the operation of this unit has been associated with the removal of scale that accumulates in the off-gas line near the reactor outlet.

Pulsed-Bed Reactors

The fluid-bed processing of uranium compounds is frequently limited when the feed material is too coarse (>20 mesh), too fine (< 200 mesh), or has a ratio of particle-size diameters greater than 5:1. Heidt and associates[2e] of the Nuclear Division of Union Carbide Corporation have employed a pulsed bed to treat uranium feed materials that are not capable of being processed in ordinary fluid beds. The original intent was to impose a large pulsing flow of gas on a small, steady gas flow, but it was observed in early work that the steady gas flow was not required. The pulses are timed so that the height of the expanded bed oscillates between 25 and 50% above the settled bed height. Use of this technique gave gas-flow rates of 4 to 10 times that available in steady-flow systems. The pulsed-bed technique has been applied successfully to the conversion of very fine and highly reactive filter cake (ammonium polyuranate) to 40-μ uranium tetrafluoride powder and to the preparation of 1-μ uranium-metal powder from large metal chips. Uranium-metal powder, in which 90% of the particles are less than 1 μ in diameter, has been prepared by reacting massive metal in a pulsed-bed reactor with hydrogen at 232°C until conversion to uranium hydride is complete and then thermally decomposing the hydride to uranium powder at 540°C.

Production of Uranium Hexafluoride

Scott, Adams, and Bresee[4] have described the application of fluidization techniques to the production of uranium hexafluoride by the reaction of uranium tetrafluoride with oxygen. Engineering feasibility of the process was demonstrated at Oak Ridge National Laboratory in a continuous, 4-in.-diameter Inconel fluid-bed reactor. The process involves the oxidation of UF_4 with air or oxygen at 800 to 850°C according to the reaction $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$. Greater than 90% of the theoretical yield of UF_6 was achieved in continuous tests with UF_4 feed rates up to 1600 g/hr.

The process for producing UF_6 from UF_4 by the use of oxygen must include a method for recycling the solid uranyl fluoride (UO_2F_2) by-product. A possible method for recycle (Fig. V-2) involves the reduction of UO_2F_2 to UO_2

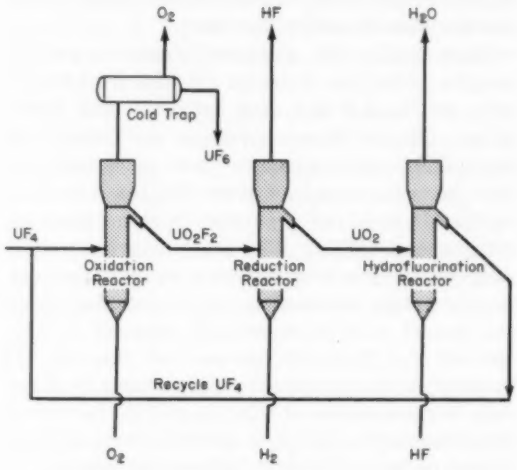

Fig. V-2 Process chemical flow sheet for UF_6 production from UF_4 with oxygen. [Reprinted by permission from Ind. Eng. Chem. Process Design Develop., *3(3): 267 (July 1964); reproduction is forbidden without permission of the copyright owner, the American Chemical Society.]*

with hydrogen and the hydrofluorination of UO_2 to UF_4, which is then recycled to the oxidation step.

This process offers an alternative method for producing UF_6 which does not involve the high cost and handling problems associated with the use of fluorine. The authors[4] suggest that this process might be economically attractive in the production of UF_6 in new small-sized facilities.

Production of Uranium Dioxide

Reduction of Uranyl Chloride in Fused Salts

The process of electrodepositing coarse crystalline uranium dioxide by reduction of uranyl chloride dissolved in a fused chloride electro-

lyte has been studied for application to the preparation of crystalline uranium dioxide as a power-reactor fuel. To be suitable for use in a reactor, uranium dioxide should have a large crystal size, high density, and an oxygen-to-uranium ratio of less than 2.015. Benedict and associates[5] have described the work performed at Hanford Atomic Products Operation (HAPO) on the preparation of reactor fuel oxides from molten chloride salt solutions.

High-quality UO_2 has been prepared by electrolytic reduction of uranyl chloride from NaCl-KCl, $PbCl_2$–2.5 KCl, and LiCl-KCl salt solutions. Of the three solutions evaluated, the LiCl-KCl system appeared to be most suitable. The main disadvantage of the NaCl-KCl system is that it requires a relatively high operating temperature (700 to 800°C), which causes (1) reduced recovery of uranium as UO_2, because at these temperatures an appreciable portion of the uranyl ions is chemically reduced to UCl_4 through reaction with carbon and chlorine, (2) formation of nonstoichiometric oxides by thermal decomposition of UO_2Cl_2, and (3) increased corrosion of the graphite anodes by the oxidizing gases in the system. In pilot-plant studies on the NaCl-KCl system, significant chlorine corrosion was observed on metal surfaces in the electrolytic cell and in the off-gas system. Although the use of the $PbCl_2$–2.5 KCl system permitted operation at significantly lower temperatures (around 580°C), the volatilization of $PbCl_2$ created major operating problems by plugging of off-gas lines, and this melt, therefore, was considered undesirable for large-scale applications. The LiCl-KCl system offers the advantages of operation at low temperatures (530 to 600°C) and very low salt volatility.

A detailed description of the pilot-plant facility for producing high-density UO_2 at HAPO and details of the effects of processing parameters on UO_2 density were presented in a previous issue of *Reactor Fuel Processing*.[6]

A typical operation[5] on an 80-liter scale, using the equimolar LiCl-KCl system, involves melting 160 kg of the salt mixture in a fused-silica crucible and drying the mixture for several hours with HCl gas. The electrolyte is prepared by the direct chlorination of U_3O_8 in the molten salt at 600°C. About 55 kg of U_3O_8 are fed to the crucible in 14-kg batches at 4-hr intervals. Chlorine is introduced through sparge tubes to give a total flow rate of 6 liters/min. The rates at which U_3O_8 and chlorine are introduced to the crucible must be carefully regulated to avoid crust formation on the pile of oxide in the bottom of the crucible and to avoid the concomitant decrease in U_3O_8 dissolution rate. The dissolution of U_3O_8 requires about 24 hr with about three to four times the stoichiometric requirement of chlorine. After dissolution is complete, HCl gas is introduced to the cell for several hours to complete the drying of the salt, i.e., to remove oxide and hydroxide constituents from the melt, the presence of which leads to high oxygen-to-uranium ratios in the electrodeposited UO_2 crystals.

An alternative procedure that has been used to obtain solutions of uranyl chloride involves the dissolution of $UO_2Cl_2 \cdot H_2O$ directly in the molten salt. This procedure avoids the lengthy dissolution time and the use of chlorine, but the drying time is increased significantly.

When the melt is sufficiently dry, graphite electrodes are lowered into the melt. Graphite is used for both the anode and cathode. Full utilization of the cathode area is achieved by using two anodes, each with an area equal to that of the cathode, placed so that one is on each side of the cathode. The electrolytic reduction is conducted at 530°C with current densities ranging from 0.1 to 1.0 amp/cm^2 and with cell voltages up to 1.8 volts. Between 24 and 48 hr are required to produce 45 kg of UO_2 in the pilot-plant cell. The UO_2 electrodeposited from the LiCl-KCl system at 530°C under optimum conditions has consistently exhibited a high density ($\geq$10.9 g/cm^3). The oxygen-to-uranium ratio has been within the range 2.0006 to 2.005. The contents of selected impurities in electrolytic UO_2 that has been thoroughly washed with water are: carbon, 20 ppm; lithium, 15 ppm; potassium, 80 ppm; and chloride, 200 to 300 ppm.

Chauvin and Coriou[7] have also observed that high-density UO_2 crystals can be prepared by electrolytic reduction of uranyl chloride from a LiCl-KCl system at 450 to 550°C. The electrolyte used in this study contained 50 wt.% UO_2Cl_2 dissolved in the LiCl-KCl eutectic (59 mole % LiCl). Chauvin and Coriou used an electrolysis procedure that was, in general, the same as that developed at HAPO. The authors investigated several materials for use as the cathode and observed that, although nickel and Inconel did not significantly contaminate the UO_2 product, these materials were severely corroded at the liquid-gas interface. Inconel apparently cor-

roded by virtue of selective removal of chromium from the alloy. Molybdenum not only was severely attacked during electrolysis but also contributed significantly to contamination of the UO_2 product.

The UO_2 product was a high-density (10.7 to 10.9 g/cm^3) crystalline material with an oxygen-to-uranium ratio of 2.00 to 2.01 and a particle size from 0.4 to 3 mm.[7] The UO_2 crystals generally possessed a lamellar structure, with the growth axis perpendicular to the cathode. Considerable difficulty was experienced in removing the electrolytic deposits from the cathode, and further work is planned to evaluate techniques for processing the UO_2 product.

Naumann and coworkers[8] have developed a method for producing coarse uranium dioxide particles by reduction with carbon monoxide of a uranyl chloride solution in an alkali chloride melt. The procedure involves passing carbon monoxide, saturated with water at 20°C, through a molten KCl-NaCl solution containing 30 wt.% UO_2Cl_2 at 700°C. The uranium dioxide forms as fine particles with a density 89% theoretical and a particle size 70% greater than 63 μ. Preliminary tests were also performed to evaluate the production of UO_2 by hydrolysis of uranium tetrachloride dissolved in KCl-NaCl eutectic at 700°C.

Precipitation from Carbonate Solutions

Pravdič and associates[9,10] have reported the results of studies on the electrochemical reduction of uranium(VI) in carbonate solutions to uranium(IV), as a means for producing uranium dioxide. In tests involving the reduction of U(VI) in sodium carbonate-bicarbonate solutions, specific reduction of U(VI) can be achieved with current efficiencies of over 80% by operation with a mercury cathode in the potential range between −1.20 and −1.85 volts vs. a saturated calomel electrode.[10] The reduction of U(VI) is performed so that no precipitation occurs in the electrolytic cell itself, but only a clear and stable solution of U(IV) carbonate complexes is formed. Precipitation of hydrated uranium dioxide is effected either by increasing the temperature of the solution to 60°C or by increasing the *p*H. Uranium dioxide powder is obtained by drying the hydrate in an inert atmosphere at 600°C.

Since the preparation of ceramic-grade uranium dioxide requires that the material be free from sodium, the electrochemical reduction technique was extended to ammonium carbonate systems.[9] Uranium dioxide with an oxygen-to-uranium ratio in the range of 2.04 to 2.09 was prepared from ammonium carbonate solutions, using the procedure established previously with sodium carbonate systems. The oxygen-to-uranium ratio in the UO_2 product was observed to be independent of the extent of reduction. Sintering of the uranium dioxide product resulted in material with a density not greater than 10.2 g/cm^3.

In other work, Pottier and Claus[11] have investigated the catalytic hydrogen reduction of alkaline uranyl carbonate solutions as a means for producing hydrated uranium dioxide. The utilization of electrolysis as a source of hydrogen offers the advantage that the relative concentrations of carbonate and bicarbonate ions in solution are not affected during the reduction process.

Sintering Properties of Uranium Dioxide

Most water-cooled water-moderated nuclear power reactors utilize sintered uranium dioxide as the fuel. This fuel must be of high density (>93% of the theoretical density) to assure dimensional stability of the fuel and a high degree of fission-gas retention. Uranium dioxide powders are produced by several different methods, and the sintering properties of the powders are determined by the method of preparation. Considerable attention has been directed toward the development of sintering techniques that would assure a high-density product from all types of UO_2 feed material.

Jakobsen and Aas[12] have applied statistical quality control to the manufacture of sintered uranium dioxide pellets for use in nuclear reactors. Careful control of the production variables was necessary to meet the density and diameter specifications that called for a minimum density of 10.35 g/cm^3 and a tolerance limit of ± 0.05 mm on the diameter. The process involved blending UO_2 powder with a lubricant and pressing the mixture to form green pellets that were subsequently sintered to high density in hydrogen. Application of quality-control methods revealed the existence of a systematic error that was attributed to the hydraulic press. The source of the error could be corrected. The control chart also indicated that, even without such correction, the press would deliver green

pellets with densities within the tolerance limits established by the specifications for the sintered product. Through the application of statistical quality-control procedures, it was recognized that the process inherently has the capability of producing pellets within much closer limits than normally required. Tolerance limits of ± 0.025 mm appear feasible if the control limits can be properly established on the basis of prior performance tests in which the sintering characteristics of the uranium dioxide feed have been evaluated.

Compared with conventional hydrogen sintering, the use of slightly oxidizing atmospheres in the high-temperature stage of the UO_2 sintering cycle appears to offer the advantage of reducing both the temperature of the sintering operation and the time necessary to attain a certain fired density. Among the possible atmospheres of this kind, steam has been widely investigated and has been shown to have merit. The effects of steam sintering of UO_2 were discussed in a previous issue of *Reactor Fuel Processing*.[13] Amato and associates[14] have evaluated steam sintering of UO_2 bodies to determine whether this technique shows sufficient advantages over conventional hydrogen sintering to be recommended for use in the production of UO_2 nuclear fuel elements. Although the advantage of steam sintering over hydrogen sintering in reducing both the soaking time and required sintering temperature was confirmed, several observations indicate that steam sintering does not offer much promise in the production of dense UO_2 bodies. Steam sintering tends to emphasize differences in properties among different UO_2 powders, whereas hydrogen sintering, by comparison, minimizes the differences. Certain powders sinter very poorly in steam. The application of steam sintering to large-scale production facilities would be complicated by the very limited choice of materials for the fabrication of the sintering furnace. At appropriate sintering temperatures (about 1400°C), ceramic materials would be required because no metals appear suitable.

In this study[14] it was shown that the core of hydrogen-sintered pellets was invariably less dense than the skin, whereas no differences in density were observed with steam-sintered pellets. The nonuniformity in density obtained during hydrogen sintering was attributed[15] to the oxidation of the pellet core by air trapped within the pressed pellet and sintering of the oxidized core before hydrogen can reduce the material to uranium dioxide. In steam sintering the uranium oxide already is partly oxidized, and a uniform composition is maintained throughout the pellet; therefore no density differences are observed.

Amato and associates[16] have also investigated the use of carbon dioxide as a sintering atmosphere in the production of high-density UO_2 pellets. Pellets of considerably higher densities were attained by sintering in a CO_2 atmosphere at 1200 to 1450°C than by sintering in a hydrogen atmosphere in the same temperature range. No carbon was detected in the final product, and the oxygen-to-uranium ratio could be reduced to nearly 2 by cooling the UO_2 compacts in a hydrogen atmosphere after CO_2 sintering. It was observed that the addition of organic binders to the UO_2 powder lowered the final sintered density.

Production of Uranium Metal

In a review of the chemical processing and metallurgy of uranium, Bellamy and Hill[17] have described the methods used in the commercial production of uranium metal. A significant feature of the text, which also discusses the metallurgy of thorium and beryllium, is the extensive coverage of metal-fabrication techniques.

Conway and Campbell[18] have described the experiences of the Watertown Arsenal in regard to the production, fabrication, accountability, and safety practices employed in the production of high-strength high-density uranium alloys from natural or depleted uranium.

The American Standards Association[19] has recently published a standard for radiation-protection features which should be incorporated in the design of installations for the fabrication of nuclear fuel and for the practices which should be followed to control radiation exposures during the operation of these facilities. This guide is specifically directed toward plants involved in the processing of natural and enriched uranium, thorium, and plutonium.

Electrolytic Processes

High-quality uranium metal has been produced at the U. S. Bureau of Mines[20] by electrolytic reduction of uranium dioxide in molten

fluoride melts at 1200 to 1300°C. In the reduction, uranium dioxide is first transformed to soluble U^{4+} ions by reaction with carbon at the anode; the U^{4+} ions are subsequently reduced to metal at the cathode. The cell reactions may be represented as

Anode reaction: $UO_2 + 2C \rightarrow U^{4+} + 2CO + 4e^-$

Cathode reaction: $U^{4+} + 4e^- \rightarrow U$

Experimental work was directed primarily toward the demonstration of a method for continuously feeding uranium dioxide to the electrolytic cell as an alternative to feeding the oxide in a consumable graphite anode. If a continuous feed is used, the high cost of preparing UO_2-carbon consumable anodes can be avoided. (Descriptions of electrolytic cells employing consumable anodes have been given in previous reviews.[21,22]) A major problem associated with continuous oxide feed to the cell is oxide contamination of the uranium-metal product. This contamination results from the fact that UO_2 is only slightly soluble in the electrolyte and also exhibits a low rate of dissolution in the melt.

Demonstration tests were conducted in 10-in.-diameter cells machined from graphite cylinders. The cathodes were machined from graphite, and high-purity carbon rods served as the anodes. The electrolyte composition was 35 wt.% UF_4, 5 wt.% LiF, and 60 wt.% BaF_2. To assure the production of a molten-metal product, the experimenters kept the temperature of the immersed portion of the cathode above the melting point of uranium (1133°C) by using high cathode current densities. Current densities of 50 to 125 amp/sq in. were used with no appreciable effects on bath temperature, fluidity, or fuming.

Several electrode arrangements were evaluated for the purpose of arriving at a configuration that would allow continuous oxide feeding and high recovery of uncontaminated metal. The most suitable arrangement incorporated a compartmented crucible with two anodes and a single cathode enclosed within a perforated graphite barrier (Fig. V-3). The perforations were vertical slits $\frac{1}{16}$ in. wide, 3 in. long, and spaced $\frac{1}{4}$ in. apart on a 120° arc. Uranium dioxide was fed continuously to the bath outside the barrier directly behind the anodes. Current efficiencies of 38% were demonstrated in tests involving the recovery of 2200 g of uranium metal. Incorporation of this cell design has significantly reduced the oxide contamination of the metal product. Carbon content of the metal, however, has remained at a high level, 740 ppm.

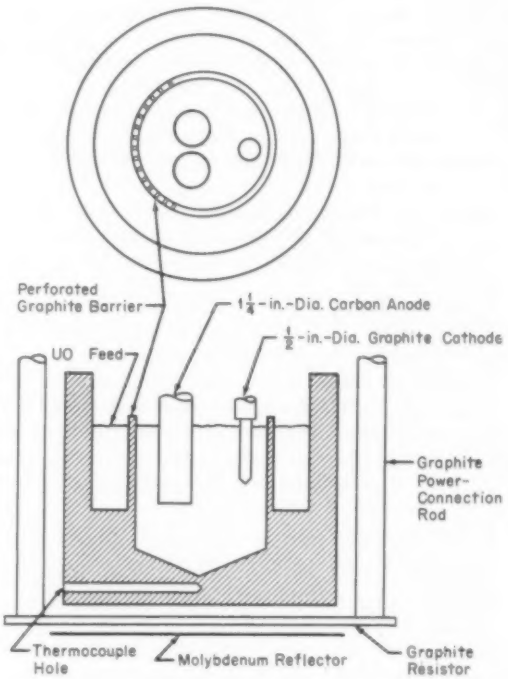

Fig. V-3 Compartmented cell for electrolysis[20] of UO_2. [From U. S. Bur. Mines Rept. Invest. 6436 *(October 1963).]*

French workers[23] have developed production techniques for supplying high-purity uranium metal by electrorefining of impure metal in fused-salt mixtures (LiCl-KCl-UCl_3) at 450 to 500°C. The apparatus has an annual capacity of 1000 kg of refined uranium. The purity of the refined metal is considered satisfactory for fundamental metallurgical studies. Most metallic impurities are present in amounts below the limit of detection. A detailed description of the electrorefining cell and the operating procedure was given in a previous issue of *Reactor Fuel Processing*.[24] (J. Barghusen)

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Section

VI

Reactor Fuel Processing

Safety in Chemical Processing

Incident in Plutonium-Processing Facility at Hanford

At approximately 1:23 a.m., Nov. 6, 1963, an incident involving a fire and the venting of an overpressured plutonium anion-exchange contactor occurred in the final plutonium-purification facility (Building 233-S) for the Redox plant at Hanford. The 233-S facility contains equipment for concentrating and loading out neptunium and for final purification of the plutonium by a moving-bed ion-exchange process. No injuries, radiation or otherwise, resulted from the incident. Details of this incident are reported here to point out certain hazards associated with the use of anion-exchange resins in plutonium service which have not been previously recognized.

Description of Plutonium-Purification Process and Equipment

The plutonium-purification step is based on the fact that plutonium is one of the few elements that form anionic nitrate complexes and therefore is readily absorbed on anion-exchange resins from nitrate solutions. In nitric acid systems the distribution coefficient for plutonium between the resin and a nitric acid solution increases with increasing nitrate concentration up to 7.3*M* HNO_3 and then decreases gradually at higher acidities. It is known that plutonium is absorbed on anion-exchange resins as the $Pu(NO_3)_6^{2-}$ complex. As the nitric acid concentration is raised from 1*M* to 7.3*M*, the increasing nitrate activity promotes the formation of $Pu(NO_3)_6^{3-}$. Above 7.5*M* HNO_3, acidic complexes are produced. At nitric acid concentrations below 1*M*, the equilibrium is reversed and plutonium can be readily eluted from anion-exchange resins.

The rate of plutonium absorption on anion-exchange resins is markedly improved by increased temperature. Although the equilibrium involving the formation of the anionic complex becomes less favorable at high temperature, the significant improvement in the reaction kinetics results in high plutonium loadings at elevated temperatures. The optimum plutonium absorption occurs at temperatures between 60 and 90°C. The operating temperature of the 233-S anion-exchange contactor was between 85 and 90°C.

The equipment used in the purification of plutonium in the 233-S facility is shown schematically in Fig. VI-1. Ozonated, steam-stripped hexone-free plutonium nitrate solution is pumped to the L-12 concentrator to prepare the solution for ion-exchange purification. The feed solution, 7*M* in HNO_3, is airlifted from the concentrator through a plutonium monitor to the ion-exchange feed tank. The solution (XAF) is then pumped to the L-18 anion-exchange contactor — a countercurrent moving-bed ion-exchange column. The contactor is a loop of 4-in. pipe divided into sections by motorized valves operated by a cycle timer. The exchange column operates by alternately introducing feed and pumping (pushing) resin. During the 15- to 30-min operating part of the cycle, the resin bed is static, and liquids flow in a clockwise direction, as shown in Fig. VI-1. Plutonium, as the anionic complex, is removed from the solution onto the resin in the extraction section of the contactor. Impurities are removed from the plutonium-loaded resin by a 7*M* HNO_3 stream (XAS) in the scrub section. Purified plutonium is eluted from the stripping section with dilute nitric acid (XCX). Stripped resin from the previous period of resin pumping drops from the resin receiver to the reservoir section of

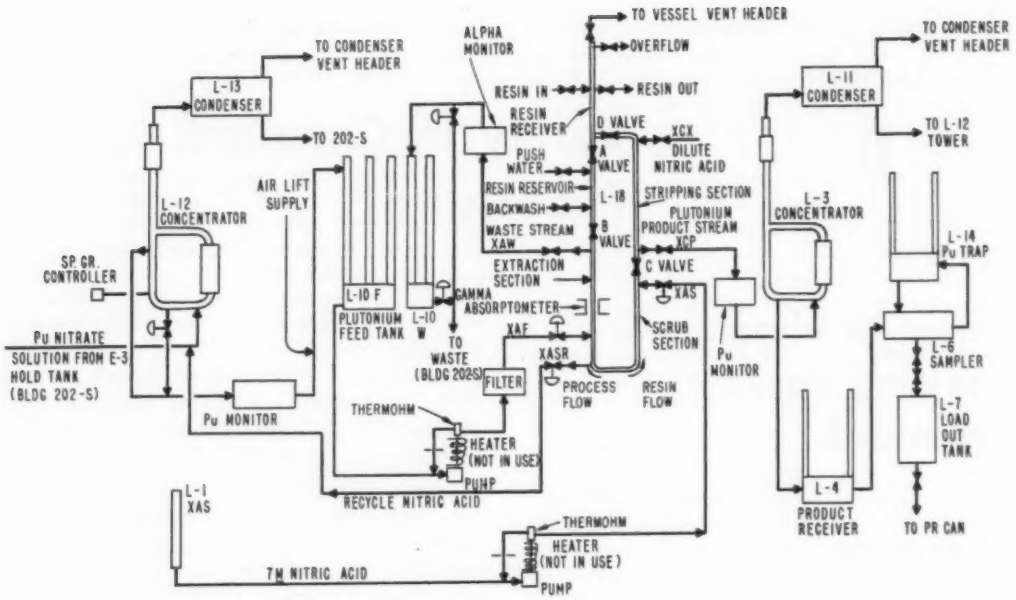


Fig. VI-1 The 233-S plutonium flow sheet.[1]

the contactor. During the 2-min push part of the cycle, all process streams are shut off and the resin is advanced hydraulically several inches counterclockwise by the addition of water to the column.

A portion of the spent scrub stream (XASR) is recycled back to the feed concentrator to conserve nitric acid. The remainder of the scrub stream, along with the depleted feed stream, leaves the contactor as waste (XAW) and is collected in the L-10W tank and eventually transferred to Building 202-S.

The plutonium product (XCP) is concentrated (L-3) by evaporation and removed through the calibrated L-7 load-out tank to product-transfer cans. Overhead vapors from the L-3 concentrator are pulled by jet into the L-11 condenser. The condensate, which contains nitric acid and plutonium carry-over, is returned to the L-12 concentrator.

All process equipment in the 233-S facility is designed to assure criticality safety by geometry for plutonium solutions at concentrations of 500 g/liter and below. Special administrative controls are used to assure that no equipment changes or personnel entries are made in the process area without prior criticality safety review and written approval. Further administrative controls are imposed on the transfer of the XAW waste stream from the 233-S building to the 202-S building. A criticality burst alarm is located in the viewing room of the 233-S facility adjacent to the process equipment.

Description of the Incident

The descriptions reported here of the incident in the 233-S facility are based on the findings of a committee formed specifically to investigate and review the event.[1,2]

OPERATION IN 233-S PRIOR TO THE INCIDENT

Early on the day shift of Nov. 5, 1963, the nitric acid scrub recycle line (XASR) became plugged. This line normally supplied about 75% of the total acid feed to the L-12 concentrator, making it possible to produce a 7*M* HNO_3 product from the concentrator without adding makeup acid to the system. With the recycle line plugged, the proper acidity in the feed solution could not be maintained, and a significant decrease in the extraction efficiency of the anion-exchange system resulted. A temporary piping connection was made in Building 202-S to permit periodic adjustment of the nitric acid concentration of the plutonium nitrate

solution in the E-3 tank. This temporary piping arrangement involved a direct tie-in to a system of two tanks with interconnected piping, one tank containing nitric acid and the other containing a solution of sodium dichromate. It was intended that nitric acid additions to the E-3 tank would be made on a regular basis, but regular additions were not made. Consequently plutonium losses in the contactor waste stream (XAW) continued at a high level.

Although proper adjustment of the nitric acid concentration in the E-2 tank was made during the next working shift (4 p.m. to midnight), plutonium losses to the waste stream still remained high. Laboratory analysis of a sample of the XAW stream, taken at 11 p.m. (approximately 2½ hr prior to the incident), indicated a plutonium concentration of 2.95 g/liter, which is more than 10 times the normal plutonium concentration. Of this plutonium, nearly 90% was found to be in the +6 valence state.

DESCRIPTION OF THE INCIDENT

At approximately 1:23 a.m., Nov. 6, 1963, a sudden reversal of air flow was noted in the 233-S building. The event was accompanied by a detectable vibration of the instrument panel board, as air from the process area was forced into the operating gallery. Immediately the operation in the 233-S facility was shut down remotely. Approximately 30 min after the first event, radiation monitors investigating the incident noted the presence of a fire. It was considered advisable by the operators that the firemen not use water in combating the fire, unless absolutely necessary, because criticality control was a consideration in the system. Only dry chemical extinguishers (sodium bicarbonate) were permitted in combating the fire. The fire was extinguished in 1½ hr by the use of approximately 500 lb of sodium bicarbonate. It was estimated later that if water fog had been used, the fire could have been extinguished in 5 min.

The fire progressed through open floor gratings to involve all four floors of the facility and the anion-exchange contactor enclosure. This enclosure consisted in part of rigid plastic panels, stainless-steel panels, plastic gloves, and other plastic units. Also involved in the fire were clothes hampers and contaminated laundry and waste materials located in the viewing room adjacent to the process area. As a consequence of the fire, alpha contamination was widely spread throughout the building.

Because of fire damage to the building and equipment, and because of the alpha contamination and the cleanup required, plus normal maintenance, the Redox plant was shut down for approximately six weeks. Operation was resumed without the use of the anion-exchange contactor and will continue indefinitely in this manner.

Analysis of Evidence and Findings

A key objective in evaluating the incident was to establish the relation between the pressurization (reversal of air flow) and the fire. At the time that the Redox plant resumed operation, it was found that the ion-exchange contactor was directly involved in the incident.

EXAMINATION OF THE ANION-EXCHANGE CONTACTOR

The anion-exchange contactor was made of 4-in.-diameter stainless-steel schedule-10 pipe. The elbows and flanges were constructed from schedule-40 pipe, whereas the interconnecting tees were schedule-10 pipe.

Examination of the contactor revealed that the stainless-steel sections in the lower portion of the contactor between the *B* and *C* valves (see Fig. VI-1) showed a uniform pipe-diameter expansion due to internal pressures. The expansion involved an increase in diameter from a nominal 4½-in. outside diameter to 4⅞-in. outside diameter, with a decrease in wall thickness. Calculations indicated that the minimum internal pressure required to permanently deform schedule-10 pipe was 1000 to 1500 psi, depending on pipe wall temperature. The schedule-40 pipe components showed no significant enlargement.

One flange gasket in the main column above the feed tee was missing completely, and a pair of Teflon gaskets on the XAW tee connection was ruptured. Screens and screen supports in two lines in the lower section of the contactor were ruptured or distorted, and three screens from widely different portions of the contactor showed discoloration, indicating exposure to high temperature. There was no evidence of any pipe rupture or of pressurization of other sections of the ion-exchange loop.

Apparently the pressure developed within the contactor at a rapid but finite rate. The rate

of pressure increase must have been low enough to allow pressure equalization throughout the loading and scrubbing sections of the column, and to allow ductile flow of the pipe wall as it yielded under pressure, so that a uniform expansion of the pipe resulted. If a detonation had occurred, the shock waves and intense local pressures would have produced uneven distension or rupture of the pipe. Instrument records support the contention that the elapsed time from the beginning of the pressure increase to the final pressure release was less than 1 min.

ANALYSIS OF THE ANION-EXCHANGE RESIN AND CONTACTOR FEED SOLUTION

An inventory of the resin after the incident established that approximately one-half of the resin remained in the column. A considerable quantity of resin was recovered from the floor of the main process area. The distribution of the resin was in a generally circular pattern of 8- to 10-ft radius, centering on the ion-exchange contactor.

Examination of resin samples removed from the column and from the floor showed that approximately 40% of the resin was degraded and possessed a sticky, gelatinous texture. The resin no longer exhibited an amber color and appeared colorless and translucent. Several of the resin beads were charred, and a few had been fractured. Resin in the vicinity of the feed tee was found to contain dichromate, and nearly every resin sample showed the presence of chromium.

A liquid sample withdrawn from the feed tank for the anion-exchange contactor showed the presence of 4.9 g/liter of Cr^{3+} and 1.7 g/liter of Cr^{6+}. This sample actually represented a blend of solution from the L-12 concentrator and the L-10F tank. The solution also contained 16 g/liter of plutonium, of which 15.2 g/liter was in the +6 valence state.

INTERPRETATION OF EVIDENCE

Pressurization of the anion-exchange contactor is believed to have been caused by chemical degradation and oxidation of the plutonium-loaded anion-exchange resin. It is suggested that the degradation of the resin may have been triggered by the inadvertent addition of sodium dichromate to the system. Dichromate appears capable of degrading resin some 50 times as fast as nitric acid in a static system at 60°C, and it is estimated that 1 to 2 hr of exposure to dichromate at 85°C would have been sufficient to produce the kind of resin degradation observed in samples after the incident.

Evidently the prolonged period of high plutonium loss to the XAW waste was directly related to the presence of dichromate to the system. Dichromate is a strong oxidizing agent which oxidizes plutonium to Pu^{6+} as chromium is reduced from Cr^{6+} to Cr^{3+}. Neither Pu^{6+} nor Cr^{3+} will absorb on anion-exchange resin; both ions will pass through the contactor to the XAW stream.

The following explanation appears to fit best the available information:

The inadvertent addition of sodium dichromate solution to the system during the afternoon or evening of Nov. 5, 1963, is considered the most likely origination of the incident. The dichromate gradually worked through the system and into the anion-exchange contactor, where it caused accelerated degradation of the resin and probably participated in an exothermic reaction, thus heating a portion of the resin above the 85°C operating temperature. At about 1:23 a.m. on November 6, a portion of resin in the vicinity of the XASR tee became hot enough to trigger the rapid pyrolysis of the plutonium and dichromate-loaded resin. Within a few seconds, the pyrolyzing resin created a localized temperature within the contactor of several hundred degrees Centigrade, and pressurized the entire load-scrub section of the contactor to more than 1500 psi by evolution of gaseous products. Schedule-10 piping in the pressurized section was expanded; the gasket in the main flange above the XASR tee then ruptured, and a high velocity stream of resin and acid sprayed out between the flange faces. The resin-acid stream ruptured containment barriers on three sides of the contactor, sprayed material rapidly to distances of 8 to 10 ft from the contactor, and caused an air flow reversal which was noted by the operators in the operating gallery. Hot gases and/or resin beads from the contactor also ignited the contaminated laundry, waste cartons, and plastic panels on the lower levels. The fire burned at low intensity until about 1:50 a.m., when it was detected by two radiation monitors and reported. Subsequently the fire increased in intensity and spread through open floor gratings to the upper levels of the viewing room. Approximately 1½ hr were required to extinguish the fire.[2]

Ignition Behavior of Anion-Exchange Resins

When the anion-exchange process was considered for plutonium-processing application,

many tests were conducted to determine the chemical and radiation stability of anion-exchange resins under conditions that would be expected to exist in plutonium production. Only a slight chemical attack of the ion-exchange resin was observed in a flowing nitric acid–plutonium system, as long as the operating temperature did not exceed 70°C. Radiation damage of the resin was found to be serious only when exposure levels exceeded 3×10^8 r. Since the plutonium-loaded resin in process application receives an exposure dose equivalent to 6×10^7 r per month, the projected useful life of the resin should be around five months. On the basis of these results, it was concluded that anion-exchange resins such as Permutit SK and Dowex 1-X4 were sufficiently stable to both chemical and radiolytic attack under the conditions that would be encountered in normal column operation to permit their use in a production facility. Accordingly, several anion-exchange systems were set up at various facilities and operated without incident for several years. However, during 1963 two accidents occurred in the United States which indicated that anion-exchange resin in plutonium service might not be as stable as previously stated. (The first incident reported involved the pressurization, followed by the rupture of a gasket and discharge of column contents, of a batch anion-exchange column at the USAEC plant at Rocky Flats in July 1963.) As a result, an experimental program has been started at Hanford to reevaluate the hazards associated with the use of anion-exchange resins in plutonium service. An accident involving the rupture of a laboratory anion-exchange column occurred in France in 1962 and is reported later.

Initial efforts in the Hanford program were directed toward determining the thermal behavior of drained resin.[1] It was observed that anion-exchange resins in the nitrate form will ignite spontaneously when heated to elevated temperatures, the temperature of ignition depending on the nature of conditioning of the resin prior to heating. In Table VI-1 resin-ignition temperatures are presented for three anion-exchange resins under several preconditioning treatments.[3] These data are for drained, but not dried, resin. There is no significant difference in ignition behavior among the three resins (Dowex 1-X4, Dowex 21K, and Permutit SK). Nitrated resin, washed with distilled water, ignites at about 200°C. Washing the resin with nitric acid lowers the ignition temperature. Resin loaded with plutonium showed a significantly lower ignition temperature than nitrate-loaded resin. The effect of dichromate on ignition temperature was not as marked. The chloride form of Permutit SK did not ignite at temperatures up to 270°C.

Table VI-1 RESIN IGNITION TEMPERATURES[3]

Treatment	Ignition temperature,* °C		
	Dowex 1-X4	Dowex 21K	Permutit SK
Nitrate resin washed with H_2O	203	215	200
Nitrate resin washed with 8*N* HNO_3	182	180	179
Dichromate-loaded resin	175	176	177
Plutonium-loaded resin	163	158	160

*Each value represents an average of two or more determinations.

Drying of conditioned resin at 90 to 110°C in air for several hours prior to heating appears to lower the ignition temperature quite markedly for both loaded and unloaded resin. Differences in ignition temperatures as great as 20°C were measured for dried and undried samples. Samples of resin loaded with plutonium and dried at 100°C ignited at temperatures as low as 138°C. Recent data[3d] indicate that the drying temperature may affect the resin ignition temperature. Drying at low temperature (less than 60°C) appears to lower the ignition temperature, whereas drying at temperatures greater than 100°C may actually raise the resin ignition temperature.

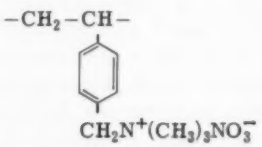
Marked differences were observed in the type of combustion resulting when loaded and unloaded resin samples were ignited. With unloaded resin, copious quantities of reddish smoke evolved from the resin container upon ignition, but no luminous flames were visible. The reacting resin remained in the sample container. When the reaction was completed, it was found that each resin particle retained its individual identity but was completely coked. The temperature in the resin bed during the reaction was not high enough to ignite the coked particles.

When the plutonium-loaded resin was ignited, a much more vigorous reaction resulted. Brightly glowing particles of resin were expelled from the sample container, and, in some instances, luminous flames were visible. The

particles of resin expelled from the container were completely burned, and only a plutonium oxide residue remained. The particles remaining in the sample container were only partly consumed and appeared to be a mixture of coke and plutonium oxide. Dichromate-loaded resin reacted in a manner similar to the plutonium-loaded samples, but visual observations indicated that the reaction was not as vigorous.

Although the tests to determine resin-ignition temperatures were carried out in air, the equipment employed in the tests was designed to limit severely the availability of oxygen to contact the resin material. The oxygen necessary for combustion is primarily supplied by the nitrated or loaded resin. Drained plutonium-loaded resin has been observed to ignite in an argon atmosphere with the same vigorous reaction as that which occurred when loaded resin was heated in air.

Permutit SK and Dowex 1 are styrene-divinylbenzene polymers containing quaternary ammonium or pyridine groups. These resins are normally supplied by the manufacturer as the chloride salts and are converted to the nitrate form by the user. The structure of the polymer unit for Dowex 1, neglecting cross-linking, can be written as



The nitrate radical supplies the oxygen required for combustion when the nitrated form of the resin is heated in the absence of atmospheric oxygen. When the resin is loaded with plutonium from a strongly acid nitrate solution, the plutonium is taken up by the resin as a hexanitrato complex, $Pu(NO_3)_6^{2-}$. For each complex ion absorbed, two nitrate radicals are displaced, and, as a result, the overall nitrate concentration on the resin is increased threefold:

$$2R^+NO_3^- + Pu(NO_3)_6^{2-} \rightarrow R_2^{2+}Pu(NO_3)_6^{2-} + 2NO_3^-$$

This means an overall increase in the oxygen available for combustion as the plutonium loading of the resin is increased. This increased availability of oxygen might account for the more vigorous reaction that occurs with loaded resin upon ignition, as compared with that of the nitrate form of resin.

In recent work at Hanford,[3] it was found that resin flooded with liquid is capable of violent decomposition. Heretofore it was believed that only drained or dried resin could be ignited. Two tests have been made which refute this premise. In one test a violent decomposition occurred in a 100-ml bomb that was half-filled with liquid-flooded resin containing thorium and dichromate. The extent of decomposition was sufficient to rupture a 6500-psi rupture disk and damage the bomb. A dichromate and 7*M* nitric acid–flooded system was also observed to produce nearly complete resin decomposition with emission of some heat and gas in a test conducted in a heated 4-in. pipe.

Workers at Hanford are currently conducting a series of experiments to determine the effect of resin volume on the ignition temperature of the resin.[3] The tests are being performed in a 4-in.-diameter by 4-ft-long pipe equipped with a rupture disk, an external electric heating system, and thermocouples on the wall and in the center of the pipe. With nitrated Permutit SK resin in the pipe, results consistently show an exothermic reaction (presumably resin oxidation), which becomes rapid enough at temperatures from 115 to 130°C to begin heating resin in the center of the pipe faster than the pipe wall is heated. Within a few minutes the exothermic reaction becomes the dominant energy source and heats the center of the resin bed to high enough temperautes (180 to 200°C) to cause violent resin decomposition. At this point the 750-psi rupture disk is blown, and most of the column contents are discharged. In only one test has a fire been produced, and in no tests has self-heating of the resin been initiated at a temperature below 115°C. Sodium dichromate does not appear to influence significantly the resin-ignition behavior in this system.

These tests have also generated data that can be employed to evaluate pressure-relief systems for controlled venting of resin decomposition reactions. Preliminary results verify that the reaction is slow enough to be vented with relative ease and that the reaction should be classified as a deflagration rather than a detonation.

Experimental work at Hanford has not yet completely reproduced the sequence of events

postulated to have occurred in the 233-S incident, but the data obtained thus far lend credence to portions of the postulated sequence. The major question that is still unresolved is what closed the gap between the 85 to 90°C operating temperature of the 233-S contactor and the threshold temperature (130°C or less) necessary for initiation of runaway self-heating inside the contactor. Future experimental work will be directed toward determining if plutonium loading of a 4-in.-diameter resin bed lowers the threshold temperature significantly and if dichromate exchange on the resin generates sufficient heat to close the temperature gap, or if some additional external source of heat is necessary.

Significance of the Incident

COSTS

The approximate cost of the incident was $397,000. This included costs for decontamination, cleanup, repainting, replacement of electrical wiring and instrumentation, replacement of process-area panels, and repair or replacement of damaged process equipment. The figure did not include indirect costs, such as diverted manpower, of $75,000. Approximately 75% of the direct cost was due to cleanup and decontamination of facilities and disposal of contaminated trash.

The extent of fire damage and the spread of contamination probably could have been reduced considerably by the use of water for fire fighting. The consensus of the investigating committee was that a prior evaluation of relative risks would have established that reasonable amounts of water fog could have been used for fire fighting with negligible risk of criticality, particularly in areas adjacent to the processing equipment. It is recommended that criteria and guides be established which will assist firemen and operating personnel in assessing the degree of criticality risk in the use of water on fires in facilities handling fissile materials.

RESIN STABILITY AND EQUIPMENT DESIGN

The most significant fact evident from the incident was the realization that the maximum safe operating temperature for plutonium anion-exchange systems is substantially lower than previously thought. Important findings are: plutonium loading markedly lowers the ignition temperature of the resin; resin flooded with liquid is capable of violent decomposition; and the resin ignition temperature appears to decrease with an increase in column diameter. The maximum safe operating temperature has not been defined, but it may be as low as 80 to 90°C. Hanford has specified a maximum operating temperature of 70°C for such systems until safe limits can be better defined.[3]

Other precautions with respect to equipment design that are considered advisable are the following:[3]

1. Provide adequate pressure relief on operating systems.
2. Incorporate hydraulic and mechanical design features in the exchange contactor to minimize the risk of forming stagnant gas pockets in the resin.
3. Establish controls to evaluate resin quality, thereby assuring that the resin does not have excessive loading capacity.
4. Establish procedures which will assure control of nitric acid concentration at a minimum practical level (7.8*M* to 8*M* maximum) and which will preclude inadvertent addition of oxidizing chemicals to the system.

(J. Barghusen and A. A. Jonke)

Rupture of Plutonium Anion-Exchange Column at Fontenay-aux-Roses

An incident involving the rupture of a glass anion-exchange column, used in the purification of plutonium solutions, occurred on June 26, 1962, in the radiochemical building at Fontenay-aux-Roses, France.[4] Plutonium is purified in small batches (approximately 10 g) from nitric acid solutions by a sorption-elution cycle, using Dowex 1-X4 anion-exchange resin. The operations at Fontenay-aux-Roses are carried out entirely in glove-box facilities.

It was the practice in the purification operation to use a pyrex-glass column 20 mm in diameter, 250 mm long, and filled to a height of 150 mm with Dowex 1-X4 resin. The resin used in this particular case had been used several times previously in plutonium service. The procedure involved passing 350 ml of a nitric acid solution (10*N* to 12*N*), containing 50 g/liter of plutonium, through the resin column to saturate the resin completely with the plutonium nitrate complex. Approximately 10 g of

plutonium was fixed on the resin. This operation was carried out at a temperature of 25°C.

Washing of the resin column with 7*N* HNO_3 in order to scrub impurities from the system was not carried out until four days after the plutonium had been loaded on the resin. At that time it was observed that the resin column was filled with small bubbles and that the color of the resin was dark brown. At the moment the operator started the wash cycle, the resin column ruptured with sufficient violence to discharge the column contents into the glove box and to inflict several cuts on the hands of the operator. The gloves worn by the operator were cut in many places by glass fragments.

On the basis of investigations made at Fontenay-aux-Roses, it appears that the accident was the result of prolonged exposure of the anion-exchange resin to high concentrations (10*N* to 12*N*) of nitric acid. As a consequence of this finding, it has been recommended that the acidity of the nitric acid solutions used in the anion-exchange purification of plutonium be limited to a maximum of 7.5*N* and that the acidity of the solutions be determined before each operation. It is also recommended that the resin-acid contact time should not exceed 24 hr, except in cases involving continuous operation. The temperature of the anion-exchange contactor should not exceed 30°C. It is suggested that the particle size of the anion-exchange resin used in plutonium purification systems be between 50 and 100 mesh. The use of resin of finer particle size may tend to induce the formation of plugs within the column which could result in localized regions of high pressure.

(J. Barghusen and A. A. Jonke)

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